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Physical, Chemical, and Biological Treatment Techniques for Industrial Wastes

Arthur D. Little, Inc, Cambridge, Mass

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PHYSICAL, CHEMICAL, AND BIOLOGICAL TREATMENT TECHNIQUES FOR INDUSTRIAL WASTES

Volume II

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Volumes I and II examine 47 unit engineering processes for their applicability to the task of treating hazardous industrial wastes.

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There is a strong need for treatment processes which can detoxify, destroy, or apply resource recovery principles to industrial wastes. This study examined 47 unit engineering processes for their applicability to the task of treating hazardous industrial wastes. Some of these unit processes are commonly used for industrial waste treatment while others require further R&D efforts before they will become commercially attractive. Four (dialysis, electrophoresis, freeze drying and zone refining) were found not to be applicable to waste treatment. Part Two of this report presents comprehensive descriptions of each of the unit processes, including information on the basic principles, areas of application, economics, energy and environmental considerations, and an outlook for future use on industrial wastes. Thus, Part Two is in essence an up-to-date reference textbook on potential treatment processes.

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FOREWORD

There is a strong need for treatment processes which can detoxify, destroy, or apply resource recovery principles to industrial wastes. This study examined 47 unit engineering processes for their applicability to the task of treating hazardous industrial wastes.

Of these unit processes, 10 can be applied for phase separation, 3 are basically for pre-processing of bulk solids or tars, 12 react chemically to destroy or detoxify the hazardous components, while 25 can be used to separate specific components within the waste stream. Some of these unit processes are commonly used for industrial waste treatment while others require further R&D efforts before they will become commercially attractive. Four (dialysis, electrophoresis, freeze drying and zone refining) were found not to be applicable to waste treatment.

Part Two of this report presents comprehensive descriptions of each of the unit processes, including information on the basic principles, areas of application, economics, energy and environmental considerations, and an outlook for future use on industrial wastes. Thus, Part Two is in essence . up-to-date reference textbook on potential treatment processes.

A major problem is how to make all of the information in Part Two readily available and useful. Section IV of Part One focuses on that problem, and is organized as a series of reference tables to be used when screening processes for application to an individual waste stream. These tables will provide a method of screening out processes that do not have any potential for the waste in question.

PREFACE

BASES FOR COST ESTIMATES

All capital cost estimates were prepared on the basis of equipment and construction costs for a time period of early 1976. The bases used were either the Chemical Engineering Plant Cost Index of 188 or a Marshall and Swift Equipment Cost Index of 450, (Reference – Chemical Engineering March 29, 1976) for all of the processes except those based on biological activity. For the biological processes, the cost basis was the Engineering News Record Construction Cost Index (ENR March 18, 1976) of 2300.

Operating labor costs were taken as $12.00/hour which was assumed to include supervision and overhead charges. Annual maintenance (labor and material) was taken as a fraction of investment and was varied according to the estimated severity of the operations. Chemicals were charged at unit prices derived from Chemical Market Reporter. Electricity was charged at $0.02/kwh.

The annualized costs of capital were established on the basis of a 10-year capital recovery factor with money borrowed at 10 percent interest. This method of annualizing capital costs has been widely used in pollution control cost estimating and is equivalent to off-the-books financing that might be obtained through the use of industrial pollution control bonds. The capital recovery factor for these cost estimates is 0.16274, i.e., the annual cost of capital is 16.274 percent of the total capital investment.

If cost estimates are to be prepared for different capacities, the following exponential scaling factors based on capacities are suggested.

Capital Investment	
All processes except biological	0.7
Biological processes	0.5
Operating Labor	0.3
Utilities and chemicals	1.0

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EVAPORATION

Prepared by

Lawrence R. Woodland

I. CONCLUSIONS AND RECOMMENDATIONS

Evaporation is a well-defined, well-established process. It is essentially omnipresent in industry. It is being used currently for the treatment of hazardous waste such as radioactive liquids and sludges, concentrating of plating and paint solvent waste, and many others. It is capable of handling liquids, slurries, and sometimes, sludges, both organic and inorganic, containing suspended or dissolved solids or dissolved liquids where one of the components is essentially nonvolatile. It can be used to reduce waste volume prior to landfill disposal or incineration.

Using steam or fuel as a heat source evaporation is energy-intensive, requiring about 100-1,100 Btu per pound of liquid evaporated. With steam cost at $4.00 per 10^6 Btu, its operating cost range, for steam alone, is $0.40 to $4.40 per 1,000 pounds of liquid evaporated. Evaporation equipment is sometimes highly specialized and thus can be expensive.

Evaporation is a Category IV process.

II. PROCESS DESCRIPTION

A. BACKGROUND

Evaporation is the vaporization of a liquid from a solution or a slurry for separation of a liquid from a dissolved or suspended solid or liquid. The term "evaporation" can only be applied to a unit operation in which heat energy is transferred to a solution or suspension of a solid or liquid and where one of the components of the substance to which heat is applied is not appreciably volatile. The process and the equipment are similar to that of the stills or reboilers of distillation except, in evaporation, no attempt is made to separate components of the vapor.

Evaporation techniques are an ancient art. Equipment for evaporation has changed a great deal during its long history, both the design and the methods of applying the necessary heat. Open, direct-fired pans were used for making salt in the Middle Ages and this method may still be used in primitive societies. Solar energy has long been used for concentrating brine in open ponds -- a technique that is still economical in some parts of the world.

The development of evaporation as a unit operation most probably evolved at the same time as the development of the chemical process industries. Today there is practically no chemical industry in which there is not some sort of an evaporation system. Most present day evaporators are heated by steam condensing on metal tubes. Nearly always, the material to be evaporated flows inside the tubes. Usually, the steam is at low pressure, i.e., below 40 lbs force per square inch absolute. Often, the boiling liquid is under a moderate vacuum -- up to 28 inches of mercury. Reducing the boiling temperature of a liquid (by reducing pressure) increases the temperature difference between the steam and the boiling liquid and thereby increases the heat transfer rate in the evaporator.

B. UNDERLYING PRINCIPLES

The objective of evaporation is to concentrate a solution consisting of a nonvolatile solute and a volatile solvent. In the overwhelming majority of evaporations the solvent is water. Evaporation is conducted by vaporizing a portion of the solvent to produce a concentrated solution or a thick liquor.

Evaporation differs from drying in that the residue is usually a highly viscous liquid, rather than a solid; it differs from distillation in that the vapor is usually a single component, and even when the vapor is a mixture, no attempt is made in the evaporation step to separate the vapor into fractions; it differs from crystallization in that the emphasis is placed on concentrating a solution rather than forming and building crystals. In certain situations, however, for example, in the evaporation of brine to produce salt, the line between evaporation and crystallation is far from sharp. Evaporation sometimes produces a slurry of crystals in a saturated mother liquor.

Normally, in evaporation the thick liquor is a valuable product and the vapor is condensed and discarded. In specific situations, however, the reverse is true. For example, mineral-bearing water often is evaporated to provide a solid-free product for boiler feed, for special process requirements, or for human consumption. This technique is often called "water distillation," but technically it is evaporation, and so it is considered here. Another situation is the case where waste streams containing solid waste, tars, slurries, sludges, or crystals are contained in a mixture of organic/organic or organic/water solvents. In this situation the solvents are evaporated off before they are distillated to separate their components. Here, the bottoms product (i.e., the wet heavy residue which could be a solid, a slurry, a sludge, or a tar-like material) must be disposed of in some manner.

C. TYPES OF PROCESSES – EQUIPMENT CLASSIFICATION

1. Special Considerations

In addition to heat transfer characteristics and economic energy utilization (i.e., steam economy), other variables which must be considered in evaporation equipment design are crystal formation, salting and scaling, product quality, corrosion, and foaming. In most cases, the associated problems can be circumvented or eliminated by proper choice of evaporator type. For instance, in the chlor-alkali industry in the concentration of sodium hydroxide cell liquors, formation of sodium chloride crystals is important. Since the quantity of salt is appreciable, it is economical to recirculate it back to the electrolytic cell for reuse. The type of evaporator chosen here has high circulation rate characteristics. Good, positive circulation in an evaporator for this purpose provides for uniformity of crystal growth and, thus, crystal size, while at the same time prevents plugging of the evaporator.

a. Salting and Scaling

This can be a real problem in evaporation equipment, causing considerable loss of heat transfer efficiency by formation of an insulating layer on the heat transfer surfaces and by an increase in the pressure drop on the liquid side. Scaling and salting may be reduced or prevented by preliminary treatment of the liquid stream, increasing the liquid velocity, careful choice of materials of construction, or by selection of special equipment such as a submerged combustion evaporator or a wiped film evaporator.

b. Product Quality

This may be another important consideration. Some criteria that this could require are low holdup time and low temperature operation to avoid thermal decomposition. It may also dictate special materials of construction for avoidance of metallic contamination or catalytic effects in the decomposition of the product.

c. Corrosion

Corrosion is another problem that may influence evaporator selection and materials construction. Corrosion and erosion are frequently more severe in evaporators than in other types of equipment because of the high liquid and vapor velocities used, frequent presence of solids in suspension, and the necessary concentration differences.

d. Entrainment

Entrainment is a liquid suspended in a vapor as fine droplets that are carried along with the rising vapor stream. The extent of entrainment losses from an evaporator depends for the most part on the vapor velocity and the size distribution of the droplets. The larger droplets may be a major source of entrainment losses unless they settle back into the liquid or are removed by entrainment separators called "deentrainment devices." Evaporators generally have devices incorporated internally or attached to a trap to remove the entrained larger droplets that do not settle back.

e. Splash-over

Splash-over consists of the carryover of large particles of thick liquor into the condenser. It occurs when boiling becomes violent and erratic. Splash-over losses are usually insignificant if sufficient distance between the surface of the boiling liquid and the outlet of the flash chamber is provided so that the liquid particles can fall back into the liquor before reaching the outlet. An alternative is an impingement baffle which covers the outlet of the flash chamber to deflect the particles downward. A single large splash-over can ruin a large volume of otherwise acceptable condensate.

f. Foam

Causes of foam in an evaporator can be organics, finely divided solids, and dissolved gases. Foam leads to an increase in entrainment by raising the effective liquid level which decreases the amount of deentrainment space and by supplying stable bubbles that vapor can carry. Foam control measures that are sometimes effective include addition of chemical anti-foam agents such as silicone preparations, baffles which the foam strikes at high velocity knocking it down, liquid or steam directed against the foam, and sudden heating or cooling of coils located in the region where the foam occurs. If a serious foam problem exists an evaporator may have to be operated at a much reduced boiling rate in order to maintain the necessary deentrainment space. If foam is anticipated, the evaporator design should provide for reserve deentrainment capacity, additional deentrainment devices, or foam breakers that will permit the desired boiling rate to be maintained without foaming.

g. Operational Capacity

In addition to the above, another consideration that must be taken into account in selecting an evaporator is operational capacity such as the amount of liquid to be treated per hour, fluctuations in volume, number of working hours per day, and volume reduction; other parameters for concern might be the case of decontamination, an important factor in the food or pharmaceutical industries, ease of maintenance, space limitations, and operating budget.

2. Evaporators — Classified by Heat Transfer Mode

a. Heating Medium Contained

A type of evaporation system where the heating medium is separated from the evaporating liquid by physical barriers. The heating medium could be confined by tubes, coils, jackets, flat plates, etc. By far, the largest number of industrial evaporators employ tubular heating surfaces. And, generally in the tubular type, the fluid to be evaporated is inside the tubes. Circulation of liquid past the heating surface may be induced by boiling or by mechanical means. In the latter case, boiling may or may not occur on the heating surface.

b. Direct Contact Evaporation

The heating medium is in contact with the liquid to be vaporized. This type includes submerged combustion flue gas contact,immersed electrode evaporation, and direct steam sparging.

c. Natural Evaporation

This type uses natural elements or phenomena to induce evaporation (e.g., solar energy or diffusion).

3. Evaporator Arrangements

a. Single-Effect Evaporators

Single-effect evaporators are used where the required capacity is small, steam is cheap, the vapors or the liquids are so corrosive that very expensive materials of construction are required or when the vapor is so contaminated that it cannot be reused. Single-effect evaporators may be operated in batch, semi-batch, continuous batch, or continuous mode.

b. Batch Evaporators

In batch evaporators, filling, evaporating, and emptying are consecutive steps. This method of operation is rarely used, since it requires the evaporator body to be large enough to hold the entire feed charge and that the heating element be placed low enough so as not to be exposed when the liquid volume has been reduced during evaporation. The more usual method of operation in a single-effect evaporator is semi-batch; here, the feed is continually added to maintain a constant liquid level until the entire charge reaches the desired concentration.

c. Continuous Batch

Evaporators of this type usually have a continuous feed and, over at least part of the cycle, a continuous discharge. One method of operating in continuous batch mode is to circulate the charge from a storage tank to the evaporator and back until the liquid in the feed tank is at a predetermined concentration, and then to proceed to evaporate to the final product concentration by finishing in small batches.

d. Thermocompression

The simplest though not the least expensive means of reducing the energy requirements of evaporation is to compress the vapor from a single-effect evaporator so that the vapor can be used as the heating medium in the same evaporator (see Figure 1). The compression may be accomplished by mechanical means or by a steam jet eductor. In order to keep the compressor cost and power requirements within reason, the evaporator must work within a fairly narrow temperature differential between the liquor and the compressed vapor, usually from -12 to -6°C. This means that a large evaporator heating surface area is required and therefore high equipment cost. There are two major uses of thermocompression evaporators in the United States. The first application is for concentration of fruit juices which are extremely temperature-sensitive. The second is in the production of fresh water from seawater.

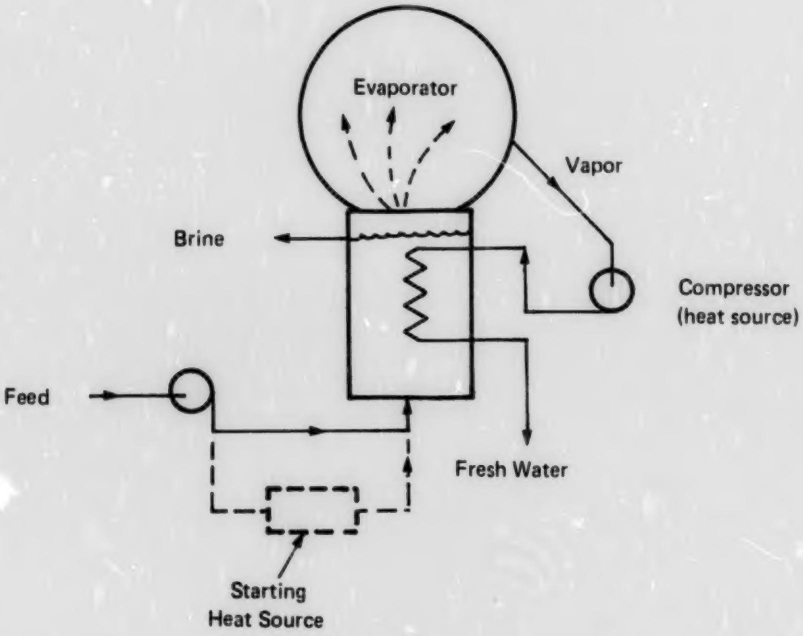


FIGURE 1 THERMOCOMPRESSION EVAPORATOR

e. Multiple-Effect Evaporation

The principal purpose for multiple-effect evaporation (see Figure 2) is for economizing on energy consumption. Most such evaporators operate on a continuous basis, although for a few difficult feeds a continuous batch cycle may be employed. In a multiple-effect evaporator, steam from an outside source is condensed in the heating element of the first effect. If the feed to the first effect is at a temperature near the boiling point of the liquor in the first effect, one pound of steam will evaporate almost one pound of water. If the vapor produced in the first effect is the heating medium of the second effect which is operating at a lower pressure than the first effect, in the second effect almost another pound of water is evaporated, which could go to a condenser; if the evaporator is a double-effect. If the evaporation is a triple-effect, the vapor may be used as the heating medium of the third effect. This may be repeated for any number of effects. Each consecutive effect operates at a lower pressure than the preceding effect.

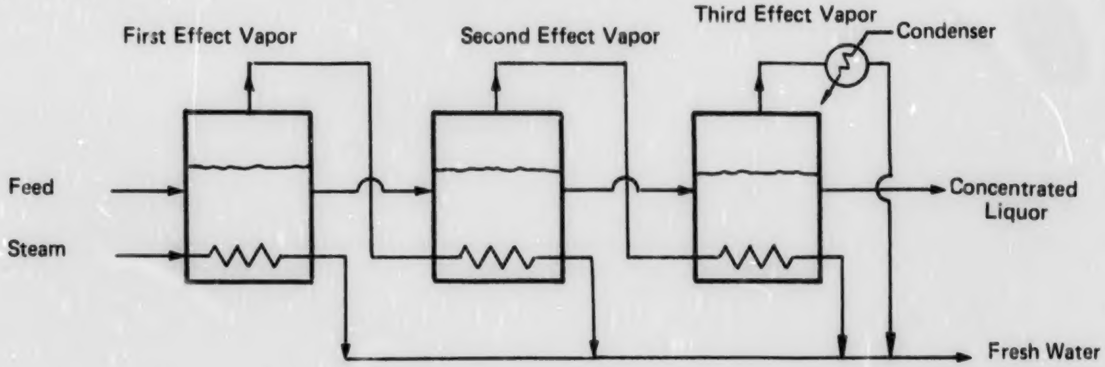


FIGURE 2 **MULTIPLE EFFECT EVAPORATOR WITH FORWARD FEED**

Large evaporators having six or seven or even up to ten effects are common in the pulp and paper industry. (See Figure 2.) The steam economy of a multiple-effect evaporator will increase in proportion to the number of effects, but usually will be somewhat less numerically than the number of effects, depending on the boiling point elevation with concentration. Recent designs for EPI use 20 effects in producing pure water from sea water, the steam-to-product ratio being 1:19, at a cost of about 35¢/1000 gallons of water. The increased steam economy of the multiple-effect evaporator is gained at the expense of the evaporator equipment cost.

To use a hypothetical example, consider a single-effect evaporator operating at a fixed steam temperature of 160°C and a final vacuum corresponding to a boiling point of 150°F. (For the sake of example, assume the feed is water.) If the feed temperature is 66°C, the evaporator will require about one million Btu/hour to evaporate 1,000 lb/hr of water. (The heat required to vaporize water is approximately 1,000 Btu/lb.) If the overall heat transfer coefficient is 200, a heating surface of 33 sq ft is required, since heat transferred (q) is equal to the overall heat transfer coefficient (U) times the heat transfer surface area (A) times the temperature (Δt) ($q = UA\Delta t$). If this evaporator is replaced by a double-effect evaporation system, the heat load in each effect will be halved. However, the total available temperature difference of 66°C will also have to be divided between the two effects. If heat transfer coefficients do not change, each effect will have the same heating surface as the single effect. Thus, the total heat transfer surface will increase in proportion to the number of effects of the evaporator. But the steam economy will have theoretically doubled since only half the steam is required to vaporize the same amount of water.

The feed to a multiple-effect evaporator is usually transferred from one effect to another in series, so that the ultimate product concentration is reached in only one effect of the evaporator. There are two modes of feeding the liquid, backward feed and forward feed.

In backward feed operation, the feed enters the last or the coldest effect. The discharge from this effect becomes the feed to the next and so on until the concentrated product is discharged from the first effect. This method of operation is generally advantageous when the feed is cold, since much less liquid must be heated to the higher temperature existing in the other effects. (The last effect is at the lowest pressure; therefore, at the lowest boiling temperature.) Backward feed is also used when the product is so viscous that high temperatures are required to keep the viscosity low enough to maintain reasonable heat transfer coefficients (i.e., high circulation rates).

In forward feed operation, raw feed is introduced in the first effect and passed from that effect to the next effect which is parallel to the flow of steam. Product is withdrawn from the last effect. This method of operation is advantageous when the feed is hot, or when the concentrated product would be temperature sensitive or would deposit scale at higher temperatures.

Forward feed simplifies operation because in most cases the liquor can be transferred by pressure difference alone, eliminating all intermediate liquor pumps. When the feed is cold, forward feed gives the lowest steam economy since the major portion of the heat content of the steam is required to heat the feed.

D. OPERATING CHARACTERISTICS

1. Feed Streams

The practical solution of an evaporation problem is profoundly affected by the character of the liquor to be concentrated. It is the wide variation of liquor characteristics that demands judgment and experience in the engineering design of evaporating equipment and in its operation. The unit operation of evaporation is thus a blend of simple heat transfer with a highly specialized engineering art. Some of the most common properties of evaporating liquids are as follows:

a. Concentration

As the concentration increases, the liquor becomes more and more individualistic for each stream or waste stream. The density and the viscosity increase with the depletion of the solvent content, until either the solution becomes saturated or the liquor becomes too sluggish for adequate heat transfer to occur. In addition, continued boiling of a saturated solution may cause crystals to form. At some point these crystals must be removed before they can settle out and cause the heat exchanger tubes to clog. The boiling temperature of a concentrated solution may be much higher (this phenomenon is called boiling point elevation) and have much higher steam requirements for vaporization of the same amount of water as it had at the more dilute level.

b. Foaming

Some materials, especially organic substances, foam during vaporization. A stable foam may accompany the vapor out of the evaporator, causing heavy entrainment of the solids. In extreme cases the entire mass of liquid may boil over the vapor outlet and be lost. The handling and/or the prevention of foam is discussed in Section II-C-1.

2. The Process and How it Operates

Since evaporation is the removal of a solvent from a solution or a slurry by boiling, heat transfer is the single most important factor in evaporator design. There are two other principal elements involved in evaporator design. These are vapor-liquid separation and energy utilization. Except in the cases where the materials to be evaporated are directly contacted (e.g., by heated vapors or by submerged combustion units), the devices in which heat transfer takes place are called "heating elements" or "calandrias." The term calandria is also used to describe a certain type of evaporator. The flow diagram of a simple evaporation system is shown in Figure 3. In the system shown, the vapor is cooled, condensed, and collected. This may not necessarily be the case.

The vapor/liquid separators are variously called "bodies," or "flash chambers." The term body is also used to denote the minimum building block of an evaporator, comprising one heating element and one vapor head. An effect is one or more bodies boiling at the same pressure.

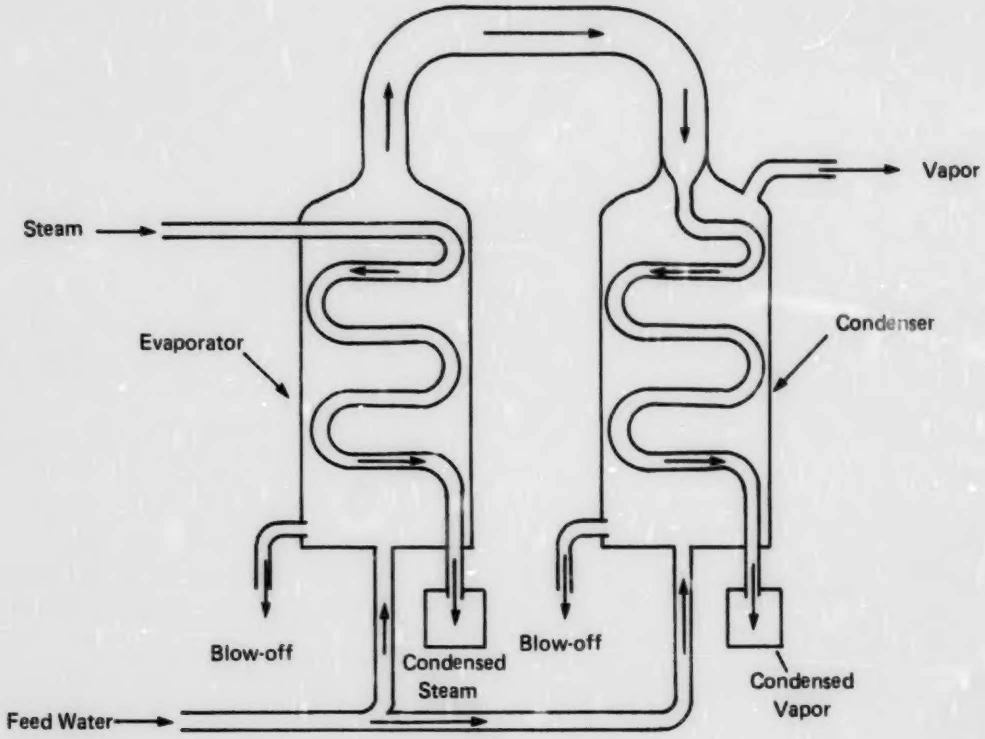

Vapor
Steam
Condenser
Evaporator
Blow-off
Condensed
Steam
Blow-off
Condensed
Vapor
Feed Water

FIGURE 3 EVAPORATOR SYSTEM

3. Out-Put Streams

Solvents being vaporized in evaporation processes are generally water, and rarely are these vapors recovered in any form. Exceptions to this are the production of fresh water from brines and the evaporation of water from solids-containing water streams for use in steam boilers. When the vapors being driven off are organics, combinations of organics, or combinations of organics and water vapor, they are normally condensed for further processing and treating, either for disposal or for reclamation.

Evaporation liquors are concentrated solutions, slurries, or slurries containing crystals. They may also be nonvolatile organic constituents such as tars or heavy polymers. Most generally, however, they are inorganic species. These liquors may contain heavy metals and other hazardous materials.

E. EQUIPMENT TYPE

1. Tubular Evaporators

The chief types of steam heated tubular evaporators in use today are discussed in the following sections.

a. Short Tube Evaporators

(1) *Horizontal Tube* – The horizontal tube evaporator (see Figure 4) was once widely used in the chemical industry but is now almost obsolete. The main use today is for power plant steam makeup evaporators. Vapor purity is of prime importance and the shell, which is a horizontal cylinder, provides the largest possible vapor/liquid separation area and thus minimizing liquid entrainment.

(2) *Vertical Tube* – The vertical tube evaporator (see Figure 5) is popular throughout industry. The body is normally a vertical cylinder. The heating surface is provided by short tubes, usually 2-3 inches in diameter. This type of evaporator has high heat transfer coefficients, providing temperature differences are large. The standard vertical tube evaporator is versatile and relatively inexpensive.

b. Long Tube Vertical Evaporators (LTV)

The long tube evaporator can be either a natural circulation type evaporator or forced circulation type. The natural circulation type LTV operates on somewhat the same principle as a smoke stack. It gives high fluid velocities, due to the velocity of the rising slugs of liquor and vapor. This, in effect, promotes higher heat transfer coefficients between the evaporating fluid and the tube walls. Sometimes, high velocities and, thus, higher heat transfer coefficients are obtained by pumping the circulating liquid around by mechanical means. These forced circulation evaporators are especially useful for evaporating viscous liquids for which natural circulation rates would be too low.

(1) *Forced Circulation (FC)* – FC evaporators are suitable for the widest variety of applications and are usually the most expensive equipment types. The FC method incorporates a circulating pump and a heat exchanger connected to a flash chamber. Heating elements in the FC evaporator can be either internal or external. FC evaporators are renowned for high velocity (8-12 ft/sec) performance and high heat transfer characteristics. They are especially applicable when expensive alloys are required and erosion is not a serious problem.

(2) *Downward Flow (Falling Film)* – The falling film evaporator is essentially an LTV evaporator turned upside-down. Feed liquor flows down the tube walls as a thin film. Friction losses of the falling film are low, thus providing better economy of energy. Heat transfer coefficients in the falling film evaporator are quite high, higher in most cases than the forced circulation evaporators. The principal difficulty in the falling film evaporator is maintaining a uniformity of feed distribution at the top of the tubes.

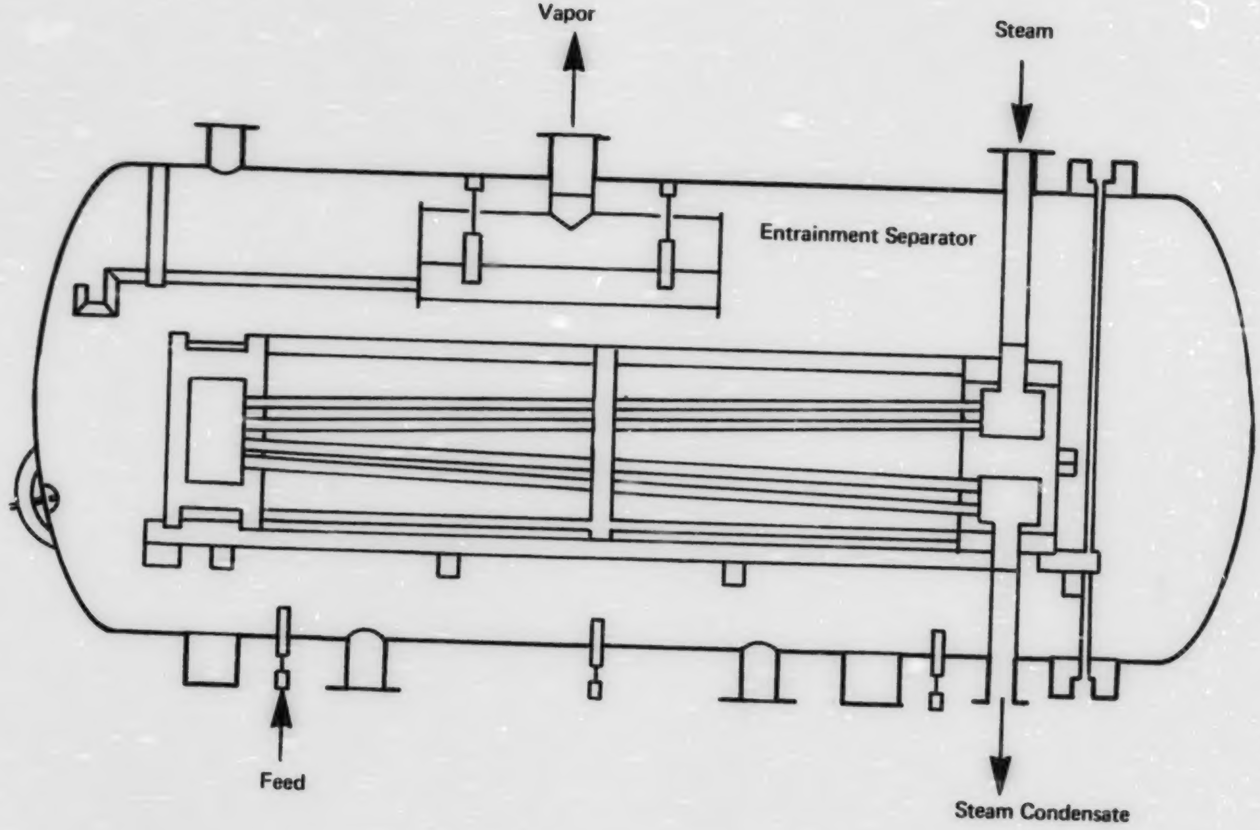

Vapor
Steam
Entrainment Separator
Feed
Steam Condensate

FIGURE 4 HORIZONTAL-TUBE EVAPORATOR

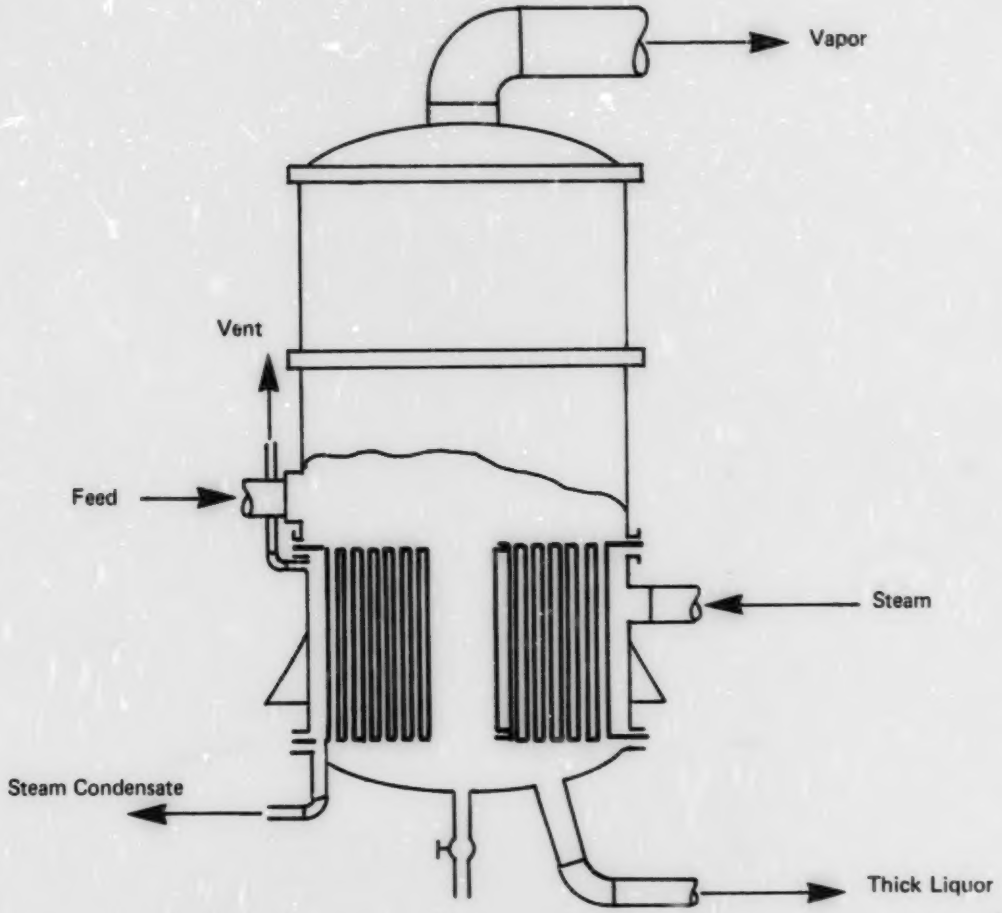


FIGURE 5 VERTICAL-TUBE EVAPORATOR

The largest number of falling film evaporators are used for the concentration of citrus juices which are heat sensitive. Another application of the falling film evaporator is for sea water evaporation where high heat transfer coefficients, small loss of working temperature difference, and low cost per unit area are important advantages.

c. Coil or Pot Evaporators

Once a popular type, the coil or pot evaporator is seldom used today but is mentioned here since it is valuable in the treatment of radioactive wastes, especially for small installations. Coil type evaporators are simple evaporators which are used particularly in simple batch operations.

2. Agitated or Wiped Film Evaporators

This type of evaporator might also be classified as a forced circulation evaporator inasmuch as it uses mechanical energy to improve heat transfer. The heating surface consists of a single tapered cylinder of large diameter with rotating blades which continue to wipe a thin liquid film on the surface of the heater. This continuous formation of a thin film permits a higher concentration of thick liquor than can be handled by any other type of evaporator.

3. Direct Contact Evaporators

a. Submerged Combustion Evaporators

In submerged combustion an oil- or gas-fired burner is immersed in a tank of solution to be evaporated. Since there is no scale formation, these evaporators are well suited to handling scale-producing or highly corrosive solutions, providing that the product cannot be harmed by carbonization. Furthermore, the economics of energy utilization are greatly improved, since heat transfer by submerged combustion is about 92% efficient; while for steam boilers, efficiency is approximately 80%. A disadvantage, however, is that evolved vapors are contaminated by combustion gases and cannot generally be recovered for reuse.

b. Flue Gas Contact Evaporators

In the cylcone-type flue, gas is admitted through a tangential inlet near the bottom of the evaporator. It flows in a whirling helical path to the top, where it exits. The liquor droplets are mixed intimately with the high-velocity gas thus providing high evaporation rates.

c. Immersed Electrode Type Evaporators

Direct contact evaporation is possible with use of immersed electrodes, but the application is extremely limited because of the high cost of electrical energy relative to fuel costs. It is applicable, however, where direct contact evaporation is required but combustion products would interfere with desired product quality.

4. Natural Energy Evaporators

a. Sludge Dewatering Beds

Because of the large volumes involved in sludge dewatering, there are sometimes serious difficulties and lack of space for disposal. The sludge removed periodically from Imhoff aerobic settling tanks is in a liquid state and, because of its volume, it is uneconomical and inconvenient to transport it to landfill disposal areas. The sludge must, therefore, be further dewatered. This dewatering step takes place in shallow excavations called "drying beds." There are a number of drying beds in any one location. They are separated from one another by concrete walls. The beds are flooded with sludge to a depth of 20 centimeters. The sludge is allowed to drain via drains and collector pipes and to dry by solar energy for a few days to a few weeks, depending upon initial solids concentration, local climate, and season of the year. In some instances, to promote faster evaporation rates, the drying beds are covered with a hood and hot air is blown across the surface of the sludge. When the solids content of the sludge is about 45%, drying is considered complete. A major disadvantage of this particular process is that relatively large areas of land are needed for the sludge drying beds.

b. Enhanced Solar Evaporation Ponds

Sometimes the solar evaporation rates in solar evaporation ponds is enhanced by use of spraying devices.

III. APPLICATIONS TO DATE

The unit operation of evaporation is practically universal to industry. Almost every industry utilizes evaporation equipment of one type or another.

Although evaporation is a relatively expensive operation requiring a large capital investment and high operating costs, it finds extensive application in the treatment of hazardous waste. This is mainly true because of the flexibility of the process, and by virtue of the fact that it is a proven, well-developed industrial process.

The process can be used for a variety of purposes including: dehydration, recovery, separation, and concentration.

In the treatment of hazardous wastes there are three basic potential uses for evaporation:

1) Where no other treatment is currently practical – i.e., concentration of TNT for simultaneous incineration.

2) Where evaporation is preferable to other methods – i.e., the concentration of radioactive wastes for disposal.

3) Where evaporation is used as pretreatment, as an integral part of a process, or as a polishing step – i.e., spent molasses mash, dye stuff wastes, and radioactive sludges.

4) For complete drying of waste waters – use furnace gases.

Specific examples of evaporation in industries and in industrial waste treatment processes (or part of a waste treatment process) are given below.

A. EXAMPLES OF PRINCIPAL INDUSTRIAL APPLICATIONS

1. The Chlor-Alkali Industry

For electrolytic caustic, commercial product concentration is a minimum of 50%. Diaphragm cell caustic (catholyte) is generally at a concentration of about 11-15% caustic soda and contains 13-15% sodium chloride.

Here, evaporation is the unit operation employed. A typical apparatus is the horizontal or the vertical tube evaporator in which the dilute caustic liquor (catholyte) in the shell side of a closed, vertical cylindrical vessel is subjected to evaporation by passing steam through the tube bundle contained in the lower portion in the vessel. Equipment configuration is multiple-effect with backward flow. The catholyte is boiled, concentrating it by driving off water vapor.

Another application of evaporation in the chlor-alkali industry is in the processing of the calcium salts. Production of calcium chloride comes about by the removal of dissolved salts where suspended matter and sulfates are removed in settling tanks by addition of barium chloride. This forms a barium sulfate precipitate. The heavy deposit of barium sulfate precipitate helps to speed up further clarification of the brine. The final stage is evaporation and crystallization of calcium chloride.

2. Saline Water Conversion Plants

There are in operation or under construction in the United States seven saline water conversion plants owned and operated by water utilities with an aggregate capacity of approximately 5 million gpd. Five of these treat brackish water by the electrodialysis process and two by multiple-stage flash evaporation processes. Saline water conversion plants are even more prevalent in other areas of the world, particularly in desert areas which are located near seas or oceans. The combined capacity of these plants is about 67 million gpd output. The largest capacity aggregate is located in Kuwait with about 20 million gpd. This includes those plants which use the electrodialysis process, but all incorporate some form of evaporation and most of them use multiple-stage flash evaporation (MSF).

3. Other Process Applications

Some other industrial process applications are listed below in Table 1.

TABLE 1

OTHER INDUSTRIAL PROCESS APPLICATIONS

General	Specific
Dehydration	Glaubers salt (salt cake)
	Sulfur sludges
Concentration	Sulfuric acid
	Hydrochloric acid
	Citrus fruit juice
	Phosphates
	Milk whey
	Natural salt brine
Crystallization	Salts: Na, K, Fe (e.g., NaCl, $NaCo_3$, KCl, etc.)
	Kaolin (for a variety of end products)
	Sugar: beet, cane, etc.
Separation & Recovery	Water from brines
	Synthetic latex solvents

B. TREATMENT OF INDUSTRIAL WASTES

1. Radioactive Wastes

Evaporators handling liquid radioactive waste require special precautionary equipment modifications. These might include special deentrainment devices, anti-splash impingement baffles, foam abatement baffles (foam abatement is also carried out using chemical additives such as surfactants).

A multi-effect evaporator system (see Figure 6) is used if a high degree of deactivation is required. An addition of an alkali to the wastewater is required to hinder the evaporation of the readily volatile isotopes and to prevent corrosion of equipment. Evaporators used at present permit concentration of the wastes to 5-10% dry residue. The concentrates are stored in buried tanks or they are dumped into the ocean. If the wastes are to be sunk, concentrates from the evaporators are used to make concrete blocks to place in steel drums.

Low activity radioactive wastes such as stormdrain runoff are handled by evaporating in a pot or coil evaporator. The evaporators are single-effect and have an extremely large vapor head and special devices to prevent foaming and entrainment.

a. Radioactive Sludges

In other radioactive waste treatment schemes, such as precipitation, a sludge is the product or byproduct. The processing and dewatering of the sludge obtained during the decontamination process poses special problems. Sludge resulting from physicochemical treatments is dewatered by evaporation or by vacuum filters. The dried sludge is stored in buried tanks similar to those for solid radioactive waste.

b. The Explosives Industry

The purification of trinitrotoluene waste is possible with evaporation and simultaneous combustion.

Two evaporation schemes are currently being employed: 1) the evaporation and combustion of wastes in spray form; and 2) multi-stage vacuum evaporation within an immersion burner.

The preliminary reduction of nitro compounds to amines using waste sulfuric acid and iron chips is another possibility. A distinct advantage for evaporation is that the evaporation and combustion steps can be carried out more conveniently and safely.

c. Photographic Chemicals

In some photographic chemical processing plants, dye waste materials are treated by a precipitation/flocculation process. The residual is centrifuged and the material from the centrifuge is further dried by evaporation for volume reduction.

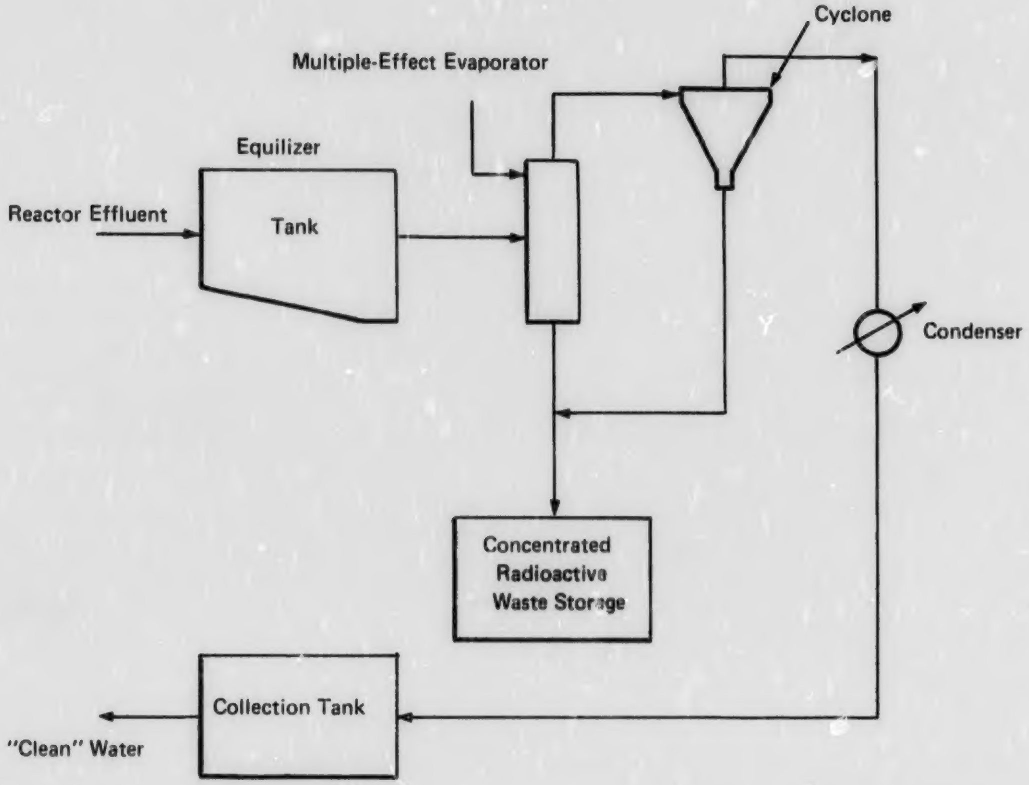

Cyclone
Multiple-Effect Evaporator
Equilizer
Reactor Effluent
Tank
Condenser
Concentrated
Radioactive
Waste Storage
Collection Tank
"Clean" Water

FIGURE 6 CONCENTRATION OF RADIOACTIVE EFFLUENTS

d. The Paper Industry

Seventy-eight percent of the pulp in the United States is produced by the Kraft sulfate process. The sulfite process accounts for another 21% and the soda process, one percent.

(1) Kraft Pulping Process – The Kraft pulping process is illustrated in Figure 7. After the wood chips have been digested, they are separated from the spent coking liquor. As the dilute "black liquor" comes from the washers, it is concentrated in a multiple-effect evaporator. The black liquor is further concentrated by the flue gas of the steam recovery furnace prior to incineration for heat and chemical recovery.

(2) Sulfite Process – In some sulfite pulp mills, after having first removed the alcohol, a direct contact evaporator is used for concentrating wastes prior to incineration.

e. Fermentation Industry – Manufacture of Molasses

The most important problem connected with the treatment of molasses distillery wastes is to deal with and make use of the spent mash. If the combined wastes are discharged to a river, then 300 kg of nitrogen, 200 kg of P_2O_5, and 1,000 kg of K_2O are lost daily in 2,000 m^3 of effluent. This spent mash is not good for fodder for cattle as it contains too many inorganic compounds. Often, the spent mash is concentrated and burned, giving a residue known as "slop carbon." The mash is concentrated in a multi-effect evaporator. From 240 tons of spent mash, about 58 tons of concentrate is obtained containing 55-59% dry solids. The concentrated slop is burned in special boiler furnaces; 58 tons yield about 90 tons of steam. The residual slop carbon contains about 43 kg of potassium carbonate per ton of molasses processed.

f. Independent Contract Waste Processors (see Table 2 for a partial listing)

In addition to the internal industrial evaporation processors for the handling of liquid or wet hazardous wastes, there are a number of independent operators who contract to handle hazardous wastes for reclamation or concentration by evaporation. One of the major applications here is for the evaporation of spent pickling liquors by solar evaporation or enhanced solar evaporation. In some cases, the bottoms are sold to municipal sewage plants as water treatment chemicals.

Tables 3 and 4 illustrate the types and forms of waste that can be handled by evaporation. Table 5 lists the residual forms after evaporation.

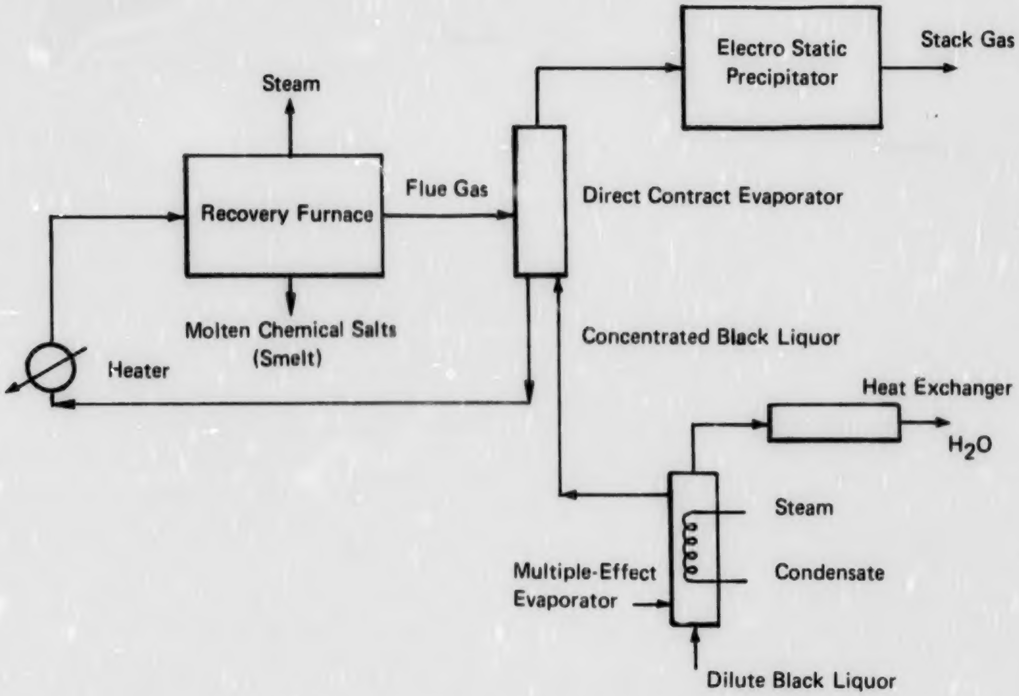

Electro Static Precipitator
Stack Gas
Steam
Flue Gas
Recovery Furnace
Direct Contract Evaporator
Molten Chemical Salts (Smelt)
Concentrated Black Liquor
Heater
Heat Exchanger
H_2O
Steam
Condensate
Multiple-Effect Evaporator
Dilute Black Liquor

FIGURE 7 WASTE LIQUOR TREATMENT AND RECOVERY FOR KRAFT PULP AND PAPER PROCESS

TABLE 2

EXAMPLES OF INDEPENDENT PROCESSORS AND WASTE TREATMENT EVAPORATION FACILITIES

Chemical Processors, Inc.
Seattle, WA

Conservation Chemical Company
Kansas City, Missouri
St. Louis, Missouri
Gary, IN

Omar Rendering Company
Chula Vista, CA

Texas Ecologists Incorporated
Robstown, TX

Waste Research and Reclamation Company, Inc.
Eau Claire, WI

Silresim Chemical Corporation
Lowell, MA

Industrial Tank, Incorporated
Martinez, CA

TABLE 3

WASTE TYPES THAT CAN BE HANDLED BY EVAPORATION

Waste Types	Yes	No	Remarks
Inorganics:			
Heavy Metals	●		Ionic in sludges and slurries
	●		Non-ionic in residues
Radioactive Materials	●		
Fluorides & Chlorides	●		Ionic – salt of light and intermediate metals
Acids		●	
Carbonyls		●	
Cyanides		●	
Organics (in nonaqueous media):			
Plain Hydrocarbons	●*		*As solvents containing solids or dissolved solids
Halogenated Hydrocarbons	●*		
Amines	●		
Nitro Compounds	●		For specific cases
Explosives	●		
Oxygenated Hydrocarbons	●*		
Sulfur Containing Organics	●		
Phosphorous Containing Organics	●		
Lead Containing Organics, etc.	●		
Metal-Organics	●		Dye stuffs, etc.

TABLE 4

WASTE FORMS THAT CAN BE HANDLED BY EVAPORATION

Waste Forms	Yes	No	Remarks
Aqueous	●		
Nonaqueous	●		
Liquid	●		
Slurries	●		
Sludges	●		
Tars	●		Special equipment (such as a dryer) is required.
Solids	●		
Dry Powders		●	
Gases		●	

TABLE 5

PHYSICAL FORMS AFTER EVAPORATION

Products	Waste Form
Overhead	Aqueous Liquid
	Nonaqueous Liquid
Bottoms	Aqueous Liquid
	Nonaqueous Liquid
	Sludges
	Tars
	Slurries
	Dry Solids in Cake, Powder or Crystalline Form

Note: Usually evaporator bottoms are wet but there are exceptions.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Energy requirements for evaporation vary with process operating parameters and equipment heat transfer characteristics. The normal operating range of energy for evaporation is about 100-1,100 Btu/lb of liquid evaporated. The average, however, falls closer to the lower end of the range when multiple-effect evaporation is used.

The energy required to evaporate a specified quantity of liquid becomes less and less, commensurate with the increase in the number of evaporator effects. The ratio of the amount of liquid which is evaporated to the theoretical amount, based on steam energy input, is called the "steam economy."

Steam economy not only varies with the number of evaporator effects but also with the quality of liquor, the solubles content, and whether there is crystal formation upon evaporation. These all have an adverse effect on steam economy.

B. ENVIRONMENTAL IMPACTS

Since in most instances the solvent being evaporated is water and providing that any entrainment or foaming problems have been taken care of in equipment operation or equipment design, there are generally no pollution problems with evaporation vapors. In the instances where vapors contain organics, the liquid vapors are generally condensed and either disposed of or are recovered by some other process such as distillation.

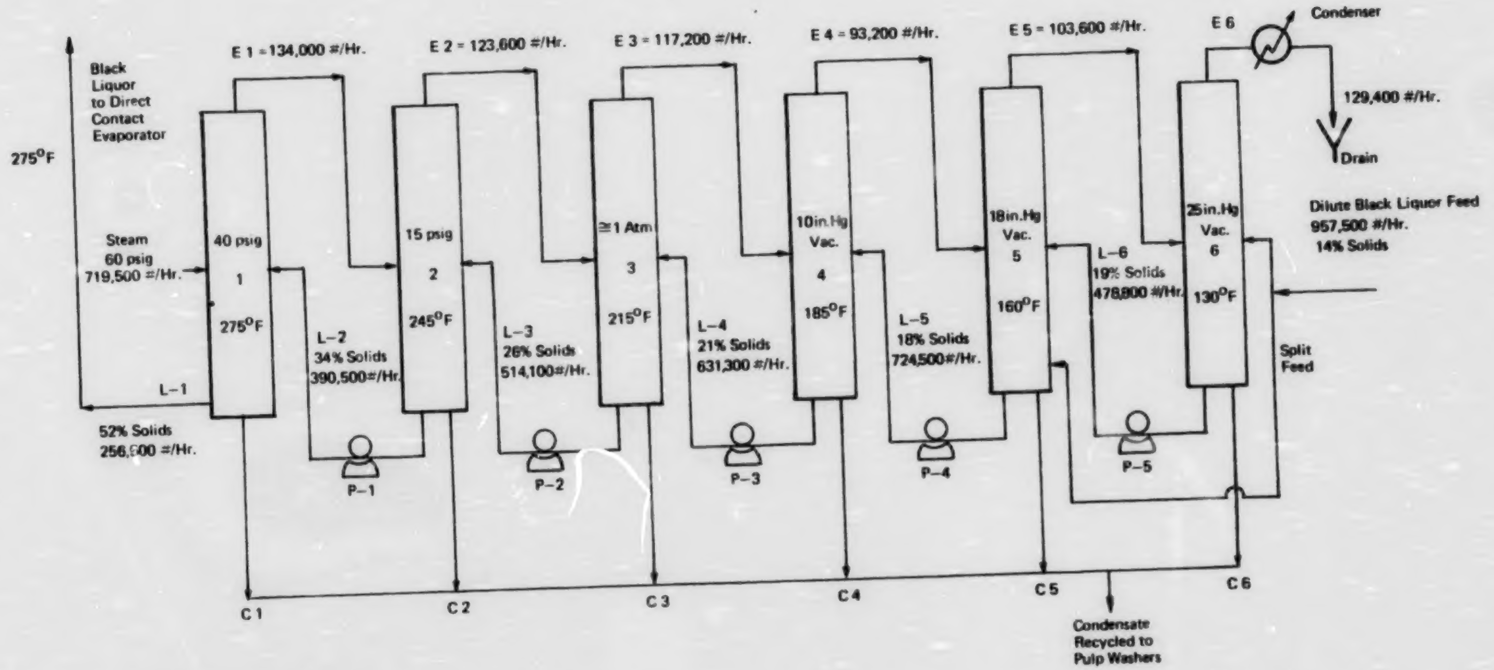
Evaporator liquors are usually considered the products. In cases where they are not in recoverable form, they must be further treated for recovery or disposed of in some manner.

C. ECONOMIC ANALYSIS

To illustrate the economics of evaporation, an economic analysis was performed on a sextuple effect evaporation system, which is typical of the type used in the concentration of kraft black liquor prior to incineration (see Figure 8). (Note: All systems for kraft liquor evaporation are quite variable and so are equipment costs. For all practical purposes the system chosen should approach the norm for systems of this type.) The system is located out of doors and is depicted in a moderate temperature zone of the United States.

1. General Costing (see Table 6)

- Cost evaluation here is made on a new equipment. The capital investment includes instrumentation, foundation, installation, painting, piping, and engineering. It does not include land value, drum filter, concentrator or storage facilities.


275°F
Black Liquor to Direct Contact Evaporator
Steam 60 psig 719,500 #/Hr.
L–1
52% Solids 256,500 #/Hr.
E 1 = 134,000 #/Hr.
40 psig
1
275°F
L–2
34% Solids
390,500#/Hr.
P–1
E 2 = 123,600 #/Hr.
15 psig
2
245°F
L–3
26% Solids
514,100#/Hr.
P–2
E 3 = 117,200 #/Hr.
≅1 Atm
3
215°F
L–4
21% Solids
631,300 #/Hr.
P–3
E 4 = 93,200 #/Hr.
10in.Hg Vac.
4
185°F
L–5
18% Solids
724,500#/Hr.
P–4
E 5 = 103,600 #/Hr.
18in.Hg Vac.
5
160°F
L–6
19% Solids
478,800 #/Hr.
P–5
E 6
25in.Hg Vac.
6
130°F
Condenser
129,400 #/Hr.
Drain
Dilute Black Liquor Feed 957,500 #/Hr. 14% Solids
Split Feed
C 1
C 2
C 3
C 4
C 5
C 6
Condensate Recycled to Pulp Washers

Material of Construction . 304SS

A–1 = 14,000 Sq. Ft.
A–2 = 14,000 Sq. Ft.
A–3 = 23,000 Sq. Ft.
thru A–6

FIGURE 8 FLOW DIAGRAM FOR SEXTUPLE EVAPORATOR SYSTEM FOR THE EVAPORATION OF KRAFT BLACK LIQUOR

TABLE 6

OPERATING COST ESTIMATES FOR EVAPORATION OF KRAFT BLACK LIQUOR IN A SEXTUPLE EFFECT EVAPORATION LOCATED OUTDOORS

Basis: Operating 24 hrs/day, 300 days/yr
Feed 957,500 lb/hr at 14% solids concentrate to 52% solids
Total water evaporated = 605 Million gal/yr (5.05×10^9 lb/yr)

Total Capital Investment: $1,300,000

	Annual Quantity	Cost per Unit	Annual Cost	
Variable Costs:				
Operating Labor	12,000 hrs/yr	$12/hr	144,000	
Utilities				
– Steam (60 lbs)	1,230,000 Million Btu/yr	$4.00/Million Btu	4,907,200	
– Electricity	746,000 kWh/yr	$0.02/kWh	15,000	
Maintenance (3% of Inv.)			39,000	
Total Variable Costs				5,105,200
Fixed Costs:				
Taxes & Insurance (2% of Inv.)			26,000	
Capital Recovery (10 yrs @ 10%)			211,200	
Total Fixed Costs				237,200
Total Annual Cost				$5,342,400
Unit Cost (cost per 1,000 lbs water evaporated)			$1.06/1,000 lb	

Source: Swenson Division of Whiting Corporation, Harvey, IL.

- Estimates were based on January 1976 using a Chemical Engineering Plant Cost Index of 188.

- The annualized costs of capital were established on the basis of a 10-year capital recovery factor with money borrowed at 10% interest. This method of annualizing capital costs has been widely used in pollution control cost estimating and is equivalent to off-the-books financing that might be obtained through the use of industrial pollution control bonds. The capital recovery factor for these cost estimates is 0.16274, i.e., the annual cost of capital is 16.274% of the total capital investment.

- Operating labor costs were taken as $12.00/hr, which was assumed to include supervision and overhead charges. Annual maintenance (labor and material) was taken as a fraction of investment. Chemicals and utilities were charged at the unit prices noted.

- Waste steam is 957,500 lb/hr of kraft liquor at 14% solids concentrated to 52%.

- Operating basis – total water evaporated is 605 million gallons per year (5.05 billion pounds). The system operates 24 hours per day and 300 days per year.

- Costs – total capital investment is estimated to be $1,300,000 (courtesy of Swenson). Of the total yearly operating costs, 96% is attributed to the cost of steam energy. The cost of evaporating 1,000 lbs of water is $1.06.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Evaporation is used mainly to concentrate a liquor where the liquor is the desired commodity. Usually, the solvent (if water) is not recovered. If the solvent is an organic, it can be recovered from the evaporator liquor in the pure state, providing the liquor contains no other volatile constituents. The role of evaporation in this type of solvent waste recovery is gaining momentum.

Solvent reclaimers use evaporation in waste solvent recovery but the major emphasis is and should continue to be internal industrial applications. This is perhaps so, since evaporation equipment is so specialized. Some industries are now recovering materials which were formerly considered as wastes. This is being done because of increased byproduct value, fuel product values, and more stringent pollution regulations.

- Development of evaporation processes with each particular recovery operation is on-going. In addition, evaporation systems are trending more and more toward energy economization such as increasing the number of effects in multiple-effect evaporators. But there are practical limitations (let alone equipment cost limitations); one of the most important is that there must be a pressure differential between successive effects which require energy for compression and vacuum. The short-term projection is that evaporation will be increasingly applied to treatment of waste streams. Most applications will be industrially captive. Some developments will be required for certain of these applications, but these will be minimized and will apply mainly to equipment arrangement with some modifications on existing design types.

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B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD

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FILTRATION

Prepared by

Edmund H. Dohnert

I. CONCLUSIONS AND RECOMMENDATIONS

Filtration is one of several well-developed liquid/solid separation processes currently being applied to the full-scale treatment of many industrial wastewaters and waste sludges. For the treatment of hazardous wastes, filtration can be used to perform two distinctly different functions:

1) Removal of suspended solids from a liquid (usually aqueous) waste stream with the objective of producing a purified liquid.

2) Increasing the solids concentration, and thereby reducing the volume, of a high concentration liquid/solid mixture (sludge) by removing liquid from the mixture (this application is commonly referred to as "sludge dewatering").

While there are a large number of commercially available filtration devices, there are but three representative types of filters generally used in large-scale waste treatment applications:

- Granular media filters – most commonly used to remove suspended solids from a liquid waste stream.

- Vacuum filters and Chamber Pressure Filters (the "filter press" – usually selected for sludge dewatering applications).

As a wastewater treatment process, filtration is usually most applicable when following some form of flocculation and/or sedimentation. As a sludge dewatering process filtration is usually technically and economically competitive with other dewatering processes.

II. PROCESS DESCRIPTION

Filtration is a physical process whereby particles suspended in a fluid are separated from it by forcing the fluid through a porous medium. As the fluid passes through the porous medium, the suspended particles are trapped on the surface of the medium and/or within the body of the medium itself. The fluid may be gaseous or liquid, but in this discussion primary attention will be focused on liquids.

The mechanisms by which the particles are removed as the fluid passes through the medium are complex. The dominant mechanisms depend on the physical and chemical characteristics of both the fluid and the particles suspended within the fluid, the physical characteristics of the filter medium, and the rate at which the fluid is forced through the medium. The type of mechanisms that predominate are thus dependent on the nature of the specific application and the type of filter employed. For example, in those filtration applications where the particles are removed on the surface of the filter medium and the particles are large, the predominant mechanism is usually simple mechanical straining. However, in those applications where the particles are small and are removed within the body of the filter medium, the mechanisms can include straining through the interstices of the filter medium, coupled with gravitational settling, diffusion, interception, and inertial impaction, all within the voids of the porous filter medium (Ref. 1). In such cases the mechanisms are greatly influenced by the dynamics of the particle/fluid flow patterns. Also important are various attachment mechanisms that affect the manner in which the particles are retained within the filter medium. These can include electrostatic interactions, chemical bridging, or specific adsorption phenomena. Often, the particles retained on or in a filter medium, will in themselves form a porour filter medium, thus altering the filtration characteristics as the filtration proceeds. While a number of mathematical filtration models based on the above theoretical mechanisms have been developed, the design of commercially available filters for specific applications is typically based largely on empirical data.

The many types of applications and process requirements have resulted in a wide variety of commercially available filtration equipment. Generally, the following features are common to all filtration systems.

- A porous filter medium.
- An induced pressure differential across the filter medium that causes the fluid to flow through the filter medium.
- A mechanical device which contains or supports the filter medium and directs and controls the flow of fluid to and from the filter medium.
- A means of removing the entrapped particles from the filter medium (alternatives can include removal and disposal of the filter medium itself).

Filter media can be divided into three general classes:

1. A thick barrier composed of a layer of granular media such as sand, coke, coal, or porous ceramics.

2. The thin barrier exemplified by a filter cloth, or filter screen.

3. A thick barrier composed of a disposable material such as powdered diatomaceous earth or waste ash.

The pressure differential required to move the fluid through the medium can be induced by gravity, by positive pressure, or by vacuum.

Most filtration applications involve the separation of solid particles from a liquid (usually acqueous) stream. Other applications can involve the separation of two immiscible liquids (such as oil and water), or the removal of particulate matter or liquid droplets from a gas stream. The intended filter application has a great influence on both the basic type of filter used and the nature of its specific physical features.

In the realm of liquid/solid separation (the most common waste treatment application), an important factor determining the type of filter used is the intended product of the filtration process. In some applications the intended product is a purified liquid stream from which suspended particles are to be removed. In other applications, the objective is just the opposite, in that solids concentrations of the mixture is already high enough so that the liquid portion is of relatively little value, and the primary objective is to concentrate the solids to facilitate handling and ultimate disposal. In aqueous systems, this process is called "dewatering of sludges." The distinction between whether the waste treatment objective is to remove solids from a liquid or liquid from solids is an important one, for it determines which class of filters can be applied.

While there are a large number of commercially available and proprietary filtration devices; in terms of basic process parameters, there are but a few representative types of filters, which are described below.

A. GRANULAR MEDIA FILTERS

Granular media filtration, one of the oldest and most widely applied types of filtration for the removal of suspended solids from aqueous liquid streams, utilizes a bed of granular particles (typically sand or sand with coal) as the filter medium. The bed is typically contained within a basin or tank and is supported by an underdrain system which allows the filtered liquid to be drawn off while retaining the filter medium in place. The underdrain system typically consists of metal or plastic strainers located at intervals on the bottom of the filter. As suspended particle-laden water passes through the bed of the filter medium, particles are trapped on top of and within the bed, thus reducing its porous nature and either reducing the filtration rate at constant pressure or increasing the amount of pressure needed to force the water through the filter. If left to continue in this manner, the filter would eventually plug up with solids. The solids, therefore, must be removed. To do this, a wash water stream is forced through the bed of granular particles in the reverse direction of the original fluid flow. The wash water is sent through the bed at a velocity sufficiently high so that the filter bed becomes fluidized and turbulent. In this turbulent condition, the solids are dislodged from the granular particles and are discharged in the spent wash water. This whole process is referred to as "back-washing." When the backwashing cycle is completed, the filter is returned to service. The spent backwash water contains the suspended solids removed from the liquid, and therefore presents a liquid disposal problem in itself. The volume of the backwash water stream, however, is normally only a small fraction (1-4%) of the volume of the liquid being filtered. Consequently, the suspended solids concentration of the backwash water is far greater than that of the liquid filtered. Granular media filtration essentially removes suspended solids from one liquid stream and concentrates them into another, but much smaller, liquid stream. Depending on the specific process configuration, backwash water itself can be treated to remove suspended solids by flocculation and/or sedimentation or by returning it to the portion of the process from whence the liquid stream subjected to filtration originated; e.g., a settling pond. A typical granular media filter is shown in Figure 1.

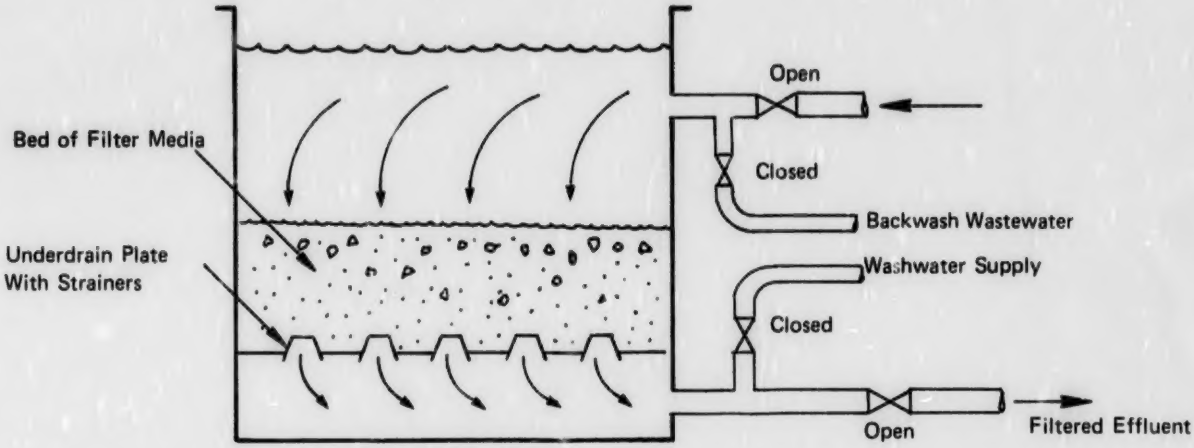
Granular media filters are primarily used to produce a purified liquid stream of low suspended solids concentration. The suspended solids concentration of the filtered liquid depends a great deal on particle size distribution, but typically, granular media filters are capable of producing a filtered liquid with a suspended solids concentration as low as 1-10 mg/liter.

While granular media filters can produce a high quality effluent with respect to suspended solids concentration, they cannot effectively filter liquids having high suspended solids concentrations. Typically, for most granular media filters to operate properly, the inlet suspended solids concentration must be well below 200 mg/liter, otherwise problems with excessively frequent backwashing are usually experienced. Very often, granular media filters are installed downstream of sedimentation processes in order to, (1) effect additional removal of suspended solids, and (2) reduce the suspended solids load on the filter by having most of the suspended solids removed in the sedimentation step.

B. FIXED MEDIA, CONTINUOUSLY RENEWED SURFACE FILTRATION

A very large number of filtration devices can be categorized under this term, including rotary drum vacuum filters, microstrainers, and disk filters. Probably the most common and most representative type of filter within this general group is the rotary vacuum filter, which is described below.

Filtration Cycle


Bed of Filter Media
Underdrain Plate
With Strainers
Open
Closed
Backwash Wastewater
Washwater Supply
Closed
Open
Filtered Effluent

Backwash Cycle

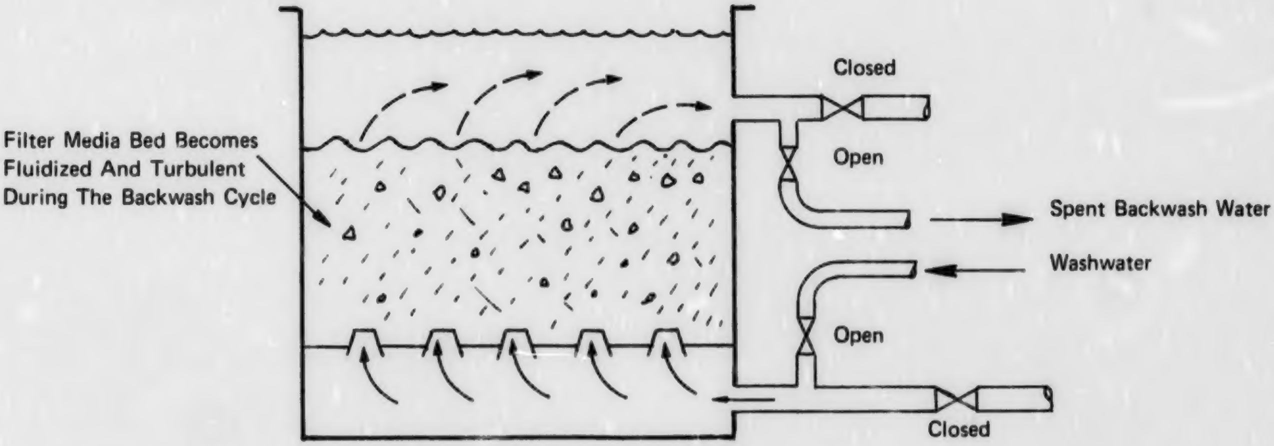

Filter Media Bed Becomes
Fluidized And Turbulent
During The Backwash Cycle
Closed
Open
Spent Backwash Water
Washwater
Open
Closed

FIGURE 1 GRANULAR MEDIA FILTER
(Cross-Sectional View)

In the rotary vacuum filter (Figure 2), the filter medium consists of a continuous belt of fabric or wire mesh. The belt is stretched over a steel cage-like drum which rotates around a central trunnion. Part of the belt sometimes revolves around a small roller. The belt-covered drum is partially submerged in a trough containing the liquid to be filtered. The drum, driven by an electric motor, slowly rotates within the trough of liquid. A vacuum is applied to the inside of the drum by means of a connection within the central trunnion. The vacuum causes the liquid in the trough (and the liquid adhering to the media as it rotates out of the trough) to be forced through the filter medium, leaving wet solids adhering to the outer surface. The filtered liquid, or filtrate, is collected from the inner bottom portion of the drum through a vacuum connection. As the belt passes over the smaller roller, a blade scrapes off the adhering solids into a collection hopper. Often, a water spray directed inward further cleans the filter media. The renewed filter surface then continues its travel and dips back into the trough of liquid. The process is continuous.

A variation of this application is the precoat vacuum filter. Typically a layer of powered material, such as diatomaceous earth, is deposited on the surface of the previously described vacuum filter as a slurry. Solids are then trapped on the surface of this layer as it rotates, dipping in and out of the trough. To prevent clogging, a thin layer of the precoat material (along with the entrapped solids) is continuously cut away by a slowly advancing blade. When the entire layer has been removed, the filter is taken out of service, given a fresh precoat, and is then ready to resume filtration. The fine pore structure of the precoat material enables much smaller particles to be removed, as compared to the unprecoated vacuum filter.

In many vacuum filtration applications, filter aids are used to improve dewaterability of certain sludges. Lime and ferric chloride are commonly used as dewatering aids. Their use improves filterability by precipitating a coating (ferric hydroxide) onto the fine sludge particles, making them larger so that they have less tendency to clog the filter media. The use of lime and ferric chloride also reduces the suspended solids concentration of the filtrate.

Vacuum filters and similar devices are primarily designed for the dewatering of waste sludges or useful products, such as TiO_2, ZrO_2, pigments, polymers, etc. They are less commonly used to produce a purified liquid stream. (For the purpose of this study a sludge is defined as a liquid stream having a suspended solids concentration greater than 2% by weight.)

The final suspended solids concentration of a sludge dewatered by vacuum filtration depends greatly on the specific sludge, but typically, the solids concentration will vary from as low as 10% to over 40%. Unless the material being dewatered is composed of relatively large discrete particles it is seldom possible to dewater a sludge by vacuum filtration to a solids concentration of much greater than 40%.

Due to the nature of the filter medium used, the filtrate from a vacuum filter typically has a suspended solids concentration of several hundred to several thousand mg/liter, and therefore, it is not usually suitable for discharge to a receiving stream without further treatment. In most cases, the filtrate is returned to the clarifier or sediment basin from

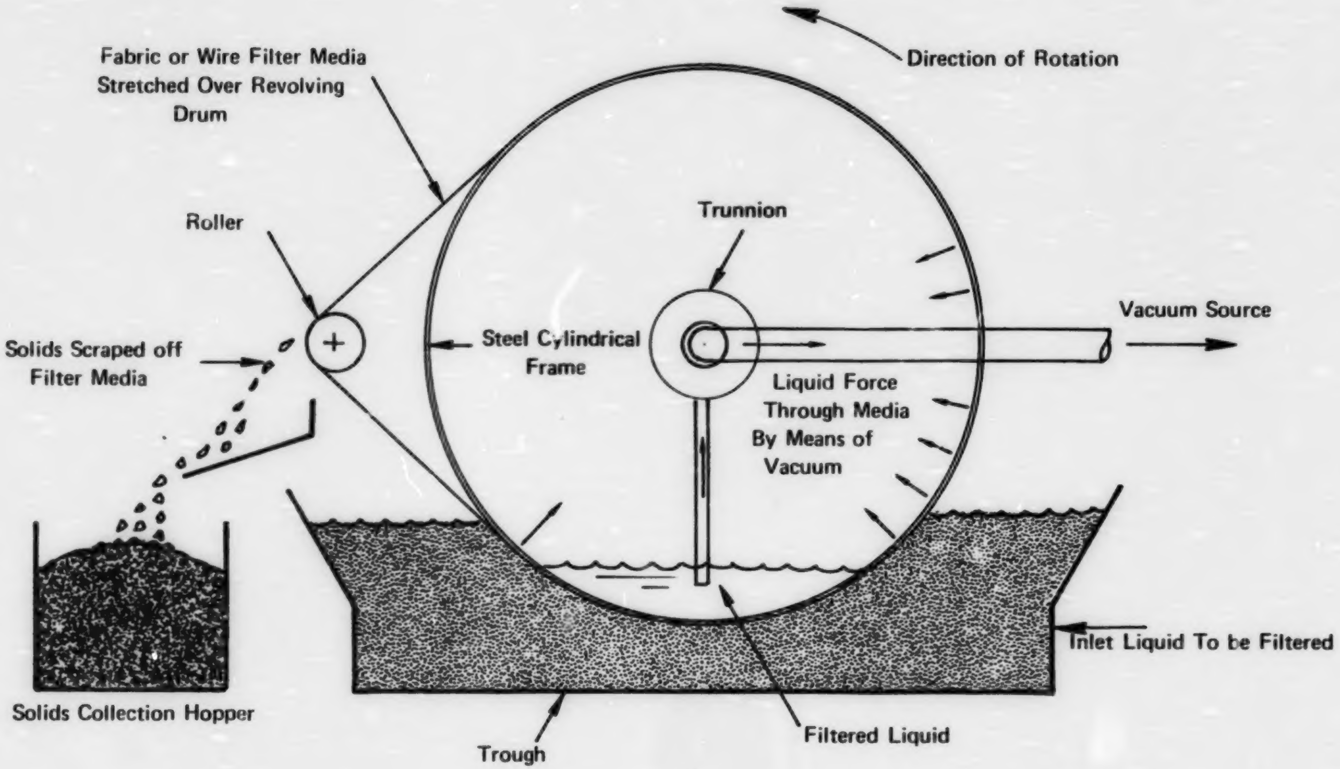

Direction of Rotation
Fabric or Wire Filter Media Stretched Over Revolving Drum
Roller
Trunnion
Vacuum Source
Solids Scraped off Filter Media
Steel Cylindrical Frame
Liquid Force Through Media By Means of Vacuum
Solids Collection Hopper
Inlet Liquid To be Filtered
Trough
Filtered Liquid

FIGURE 2 ROTARY DRUM VACUUM FILTER
(Cross-Sectional Side View)

which the sludge was drawn, where it is incorporated with the incoming waste stream to eventually become part of the sludge once more.

C. CHAMBER PRESSURE FILTERS

In one large category of filters, rigid individual filtration chambers are operated in parallel under relatively high pressure (up to 250 psi). This category includes pressure leaf filters, horizontal plate filters, tube element filters, and the plate-and-frame or so-called "filter press." The filter press is the most common and representative of this group.

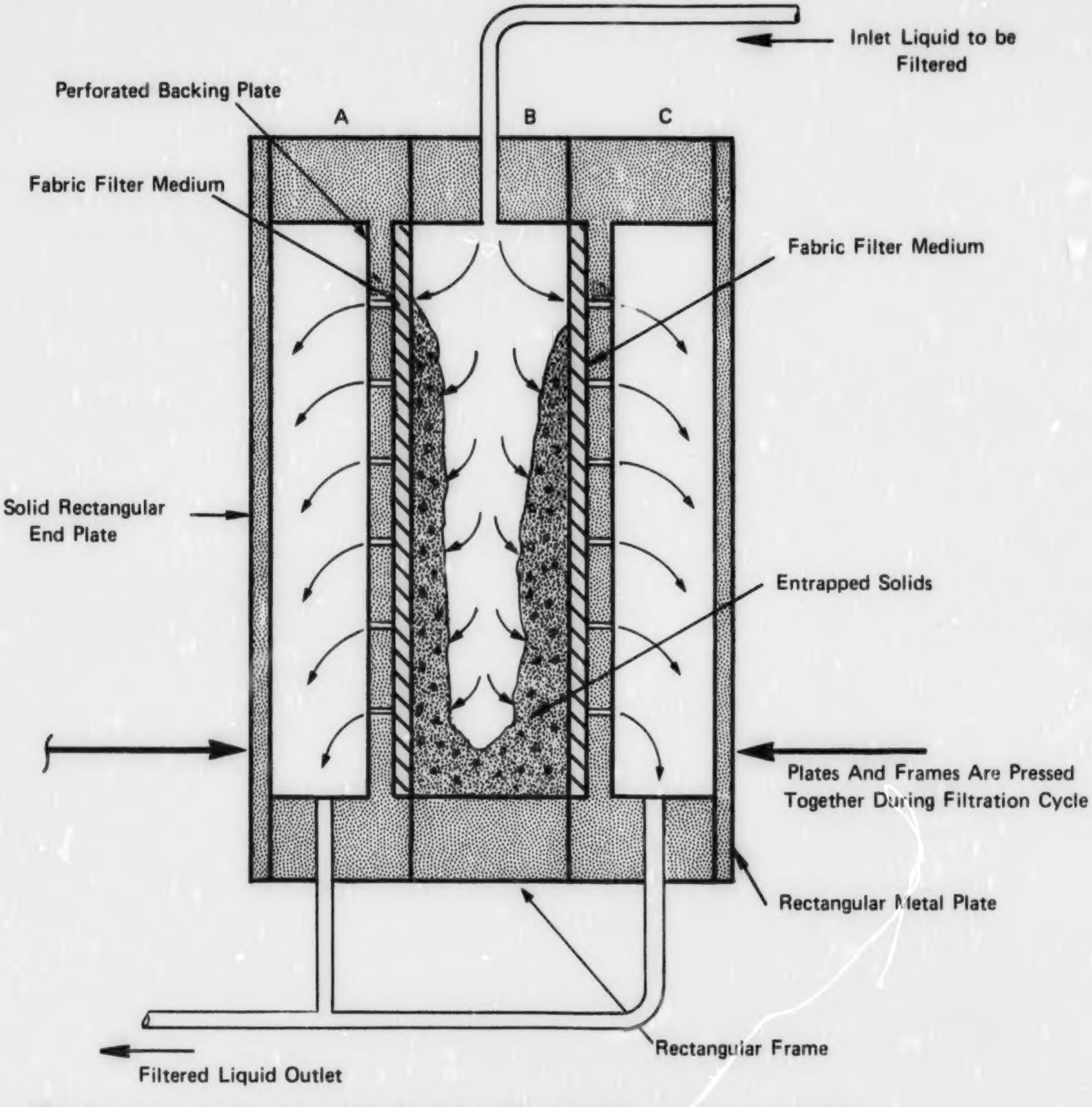
The filter press consists of a series of plates and frames, alternately arranged in a stack and "pressed" together by a large screw jack or hydraulic cylinder, hence the term "filter press." An illustrative cross-sectional view of one section of a typical plate-and-frame arrangement is shown in Figure 3.

Referring to Figure 3, the liquid to be filtered enters the cavity formed by frame "B." Pressed against this hollow frame are plates "A" and "B" which consist of perforated metal plates covered with a fabric filter medium. As the liquid flows through the filter medium, solids are entrapped and build up within the cavity. When the solids build up to a certain level, the plates and frames are separated, the solids scraped away into a receiving hopper, the media washed, and then the whole assembly is returned to service by pressing the plates together and resuming the flow of liquid.

In certain applications, the medium is covered or "precoated" with a powdered filter aid such as diatomaceous earth. As in the case of the previously described vacuum filter, the precoat material enables the removal of smaller particles. Lime and ferric chloride filter aids are also frequently used in filter press applications to effect more complete removal of solids.

In most applications the end-products of a filter press are very similar to that of a vacuum filter. The intended product of most filter press waste treatment applications is a dewatered sludge of typically 15-50% solids concentration. The by-product is a filtrate stream that, as in the case of the vacuum filter, typically contains several hundred to several thousand mg/liter of suspended solids.

In many applications, both for industrial processing and waste sludge dewatering the vacuum filter and the filter press are technically and economically in competition with each other. For waste treatment applications, vacuum filters are more commonly used, but recent improvements in filter press design have resulted in an increased use of filter presses for waste sludge dewatering. Filter presses are generally more effective in dewatering difficult-to-filter sludges of a sticky or gelatinous nature. Also, for a given type of sludge, the filter press is usually capable of producing a dewatered sludge of a higher solids concentration. These advantages over the vacuum filter are usually balanced off by slightly higher capital and operating costs.


Inlet Liquid to be Filtered
Perforated Backing Plate
A
B
C
Fabric Filter Medium
Fabric Filter Medium
Solid Rectangular End Plate
Entrapped Solids
Plates And Frames Are Pressed Together During Filtration Cycle
Rectangular Metal Plate
Rectangular Frame
Filtered Liquid Outlet

When the cavity formed between plates A and C is filled with solids, the plates are separated.
The solids are than removed and the medium is washed clean.
The plates are than pressed together and filtration resumed.

FIGURE 3 FILTER PRESS
(Illustrative Cross-Sectional View of One Rectangular Chamber)

III. APPLICATIONS TO DATE

A. INDUSTRIAL APPLICATIONS

The process of filtration is old, and rudimentary filtration devices date back to antiquity. The basic types of filtration devices previously described have been in general use throughout industry since the early 20th century. Whenever it is necessary to separate solid particles from a fluid, filtration is potentially applicable. Very often, filtration is used in conjunction with precipitation, flocculation, and sedimentation in order to improve the overall solids removal efficiency.

In considering applications, it is useful to divide filtration into two major categories, according to desired objectives:

1. Those applications in which the objective is the production of a purified liquid stream, in which the filter serves to remove solids from the liquid.

2. Those applications in which the objective is the concentration or dewatering of a slurry or sludge, in which the filter serves to remove liquid from the solids.

Generally, granular media filters are used for the production of a purified liquid, while fixed-media, continuously renewed surface filters and chamber pressure filters are used for the dewatering of slurries and sludges. Exceptions to this generalization are the precoat variations of the vacuum filter and filter press which are sometimes used to produce a purified liquid and a washed solid.

1. Industrial Manufacturing Processes

Some typical examples of the use of filtration in industrial manufacturing applications are listed below:

a) The Inorganic Chemicals Industry – Many segments of the inorganic chemicals industry employ various forms of filtration to separate precipitated product from waste material. Rotary vacuum filters are commonly used in the manufacture of titanium dioxide, sodium dichromate, aluminum sulfate, and magnesium (Ref. 3).

b) The Organic Chemical Industry – Many manufacturing operations in the organic chemicals industry employ various types of rotary vacuum filters and filter presses. In the production of acetylene, for example, carbon particles contained in aqueous quench streams are sometimes removed by means of rotary vacuum filtration (Ref. 4).

c) In the manufacture of dye materials, solid dye particles called dry colors are all recovered in filters.

d) Rotary vacuum filters are used to remove impurities in the manufacture of sugar (Ref. 6).

e) Petroleum refineries use clay slurries to remove impurities from lube oils. The clay is often removed from the product oil by means of vacuum filtration (Ref. 7).

2. Industrial Water Treatment

Both boiler feed water and many types of industrial process water have stringent specification on suspended solids. Frequently, granular media filtration, often in conjunction with precipitation, flocculation and sedimentation, is used for the removal of suspended solids.

3. Industrial Wastewater Treatment

Filtration is used as a final suspended solids removal step in many industrial wastewater treatment applications. In addition, sludges from wastewater treatment plants are frequently dewatered and reduced in volume by means of rotary vacuum filters and filter presses. Some of these applications are discussed in the following section on waste treatment applications.

B. CURRENT WASTE TREATMENT APPLICATIONS

Granular media filtration is in widespread use throughout many industries for the treatment of process wastewater. With regard to wastewater streams that can be considered "hazardous," one of the more common applications of granular media filtration is the removal of metal precipitates from wastewater after the wastewater has been subjected to precipitation, flocculation, and sedimentation. As discussed in the companion report on precipitation, flocculation and sedimentation, some hazardous materials that are commonly removed from wastewaters by precipitation are:

- arsenic
- cadmium
- chromium
- copper
- lead
- mercury
- nickel
- zinc

In many precipitation reactions (particularly in the sulfide precipitation of metals), very fine precipitates are formed which are only partially removed from the liquid stream by sedimentation. Filtration often can serve as a polishing step to improve the overall removal of the suspended precipitates. Specific examples of filtration used in conjunction with precipitation, flocculation, and sedimentation are given below:

Arsenic has been removed as the sulfide from industrially contaminated municipal wastewater by means of precipitation, flocculation, and sedimentation followed by sand and coal granular media filtration (Ref. 8).

Cadmium has been removed as the sulfide from wastewater on a pilot plant scale by means of flocculation, sedimentation and multi-media granular filtration (Ref. 9).

Chromium is typically removed from metal finishing wastewater by chemical reduction to the trivalent state followed by lime precipitation as the hydroxide, flocculation and sedimentation. Often granular media filtration is used to improve the removal of chromium hydroxide precipitates (Ref. 10).

Lead is removed from wastewater from a tetraethyl lead plant by hydroxide precipitation with lime. The precipitates, after settling are dewatered by means of rotary vacuum filtration (Ref. 11).

Mercury is effectively removed from wastewater by the reduction of mercury ions to metallic mercury by means of reaction with sodium borohydride. The metallic mercury particles are removed by filtration (either rotary vacuum or filter presses) (Ref. 12).

Nickel is removed from plating wastewater by means of hydroxide precipitation with lime. Granular media filtration can often be used to improve the removal of precipitated particles (Ref. 13).

Zinc is often removed from wastewater by means of hydroxide precipitation with lime at controlled pH followed by sedimentation. The settled precipitates are often dewatered by means of rotary vacuum filters.

Waterborne Oily Wastes are removed by various types of filtration devices in series with the more traditional types of oil separators to improve the overall oil removal efficiency.

Waste Lube Oil from automobiles, trucks, and industrial applications contain a variety of hydrocarbon compounds, many of which are considered hazardous. In addition, many of these oils also contain colloidal metal particles. The reprocessing of waste lube oil can be considered a hazardous waste treatment technique, since a volume of oil that is reclaimed is a volume of oil that is not disposed of. In the waste oil reclamation process, one of the treatment steps involves a dewaxing operation in which wax crystals must be removed from the reclaimed oil. Filtration is used for the removal of the wax crystals (Ref. 14).

Wastewater from Pesticide Manufacture is amenable to filtration (for at least a portion of the treatment) since many pesticides have a very low solubility in water. In the manufacture of the pesticide endrin (now considered a toxic substance by the Environmental Protection Agency), wastewater is treated by sedimentation and granular media filtration prior to discharge into a municipal sewage system (Ref. 15).

Air Pollution Control can be achieved using a variation of the chamber type of filter used for air pollution control is the so-called bag filter (an entire bag filter system is often referred to as a bag house). Bag filters are used for the removal of particulates from gaseous stream. Many such particulates, e.g., condensed zinc, lead oxide, and arsenic fumes, are considered quite hazardous. Bag filters are thus used both to present environmental damage and to comply with OSHA regulations.

Sulfur Dioxide Air Pollution Control Systems Most air pollution control systems intended for the removal of sulfur dioxide from stationary combustion sources use alkaline scrubbing solutions and remove the sulfur dioxide as a calcium sulfite/sulfate sludge. Vacuum filtration has been used to dewater this sludge prior to final disposal (Ref. 15).

Dewatering of Waste Sludges from Biological Treatment Systems Biological treatment is extensively used for the treatment of wastewater from the Pulp and Paper Industry, Petroleum Refining Industry, and Organic Chemicals Industry. Waste sludges from the biological treatment systems are frequently dewatered by vacuum filtration prior to land disposal or incineration (Ref. 15).

C. POTENTIAL APPLICATIONS TO WASTE TREATMENT

Whenever suspended particles are present in a fluid stream, filtration is potentially applicable to effect a separation between the particles and the fluid. The fundamental requirement is that the suspended particles either be of sufficient size or be capable of being increased in size by flocculation (see companion ADL report on "Precipitation, Flocculation, and Sedimentation") such that they can be trapped in or on the filter medium. For this reason, the basic types of filtration devices described in this report are sometimes marginally effective in removing very small truly colloidal particles, unless those particles can be made larger by flocculation. In cases where it is not possible to flocculate such particles (as in the case of many oil/water emulsions), more advanced techniques such as ultrafiltration (discussed separately in a companion ADL report) are more applicable.

Filtration is a purely physical separation process. Depending on the application, filtration can either serve as the sole liquid/solid separation process, or it can be used in conjunction with other liquid/solid separation processes (such as flocculation and/or – sedimentation or centrifugation).

Potential applications of filtration to various forms of hazardous wastes are discussed below and summarized in Table 1.

TABLE 1

POTENTIAL APPLICABILITY OF FILTRATION TO VARIOUS FORMS OF HAZARDOUS WASTES

	Potential Applicability		
Waste Form	**Granular Media Filters**	**Fixed-media, Continuously Renewed Surface Filters**	**Chamber Pressure Filters**
Aqueous	High	High	High
Non-Aqueous Liquid	Moderate	Moderate-High	Moderate-High
Slurries	Low	High	High
Sludges	Low	High	High
Tars	Not Applicable	Not Applicable	Not Applicable
Solids	Not Applicable	Not Applicable	Not Applicable
Dry Powders	Not Applicable	Not Applicable	Not Applicable
Gases	Not Applicable	Not Applicable	Moderate*

*Bag filters for particulate removal only.

1. Aqueous Liquids

As discussed in the preceding sections of this report, granular media filtration is being used to remove solid particles from aqueous waste streams and is particularly effective where a high degree of solids removal is desired. As more and tighter restrictions are placed on the discharge of heavy metals, one can expect to encounter more applications in which filtration is used after precipitation, flocculation, and sedimentation to ensure that a minimum amount of metal precipitates are discharged in the final effluent.

Depending on the suspended solids concentration of the wastewater streams, it may be necessary to install other liquid/solid separation processes such as flocculation and/or sedimentation ahead of granular media filtration in order to take the bulk of the suspended solids load off the filters.

Activated carbon adsorption is often applicable to the treatment of various kinds of soluble organic hazardous waste materials (Ref. 16). Very often the soluble hazardous material is accompanied by a large amount of relatively inert suspended solids. Activated carbon columns cannot accept large amounts of suspended solids because they are prone to become plugged. Granular media filtration, therefore, is often installed ahead of a carbon adsorption system in order to remove suspended solids. One can expect filtration to accompany activated carbon adsorption for many aqueous hazardous waste applications.

2. Non-Aqueous Liquids

Filtration is definitely applicable for the removal of suspended solids from non-aqueous liquids, provided that the liquids are relatively free-flowing and not overally viscous or adhesive. Most potential applications would involve the removal of solid particles from waste organic solvents, either in conjunction with reclamation or ultimate disposal. Filtration is necessary to produce clarity in recovered solvents which will be offered for sale. All waste fuels, destined for incineration, are filtered to remove solids and sludges which could block the burner nozzle.

3. Slurries and Sludges

In the treatment of slurries and sludges, the main function of filtration is the dewatering and resultant reduction in volume of the slurry or sludge. Volume reduction allows the waste to be contained within a smaller area and thus improves the overall disposal economics. Rotary vacuum filters and filter presses are primarily used for these applications. Since filtration is a purely physical separation process, the hazardous waste sludge or slurry will not be changed in chemical composition; it will only be more concentrated. If a sludge contains both hazardous and non-hazardous solid particles, and if these are radically different in particle size, filtration could theoretically affect some form of separation. In practice though, it is extremely difficult to selectively filter different size particles, especially if those particles are contained within a gelatinous matrix.

4. Tars

Heavy, viscous tars do not generally lend themselves to filtration, mainly due to the difficulty in cleaning the filters.

5. Solids, Dry Powders

Filtration is not applicable to the treatment of hazardous wastes that are in the form of a solid or dry powder.

6. Gases

Filtration is potentially applicable to the removal of solid particles from gaseous waste streams and is a commercial operation. Examples include:

1) The use of rigid filter media supported on rotating discs; and

2) The use of filter media in the form of bags, as in bag-houses.

As a rule, there are no air emissions from the filtration process, except in gas filtration, of course. Liquids are exposed to the atmosphere, however, and if those liquids are highly volatile or contain volatile components, air emissions could result. Nevertheless, air emissions are rarely a problem in filtration applications.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

The only energy requirement associated with filtration is the energy required to pump the fluid through the filter medium. Compared with many other processes applicable to the treatment of hazardous wastes, the energy requirements of filtration are low. For example, a vacuum filtration system capable of dewatering a 36,000 gpd sludge stream containing 6 tons of solids will typically have a total installed power requirement of only 25 horsepower.

Vacuum filters and filter presses generally consume more energy than granular media filters. In general, energy consumption is not a major factor in the selection of a liquid/solid separation process for waste treatment applications.

B. ENVIRONMENTAL IMPACTS

As a rule, there are no air emissions from the filtration process. Liquids are exposed to the atmosphere, however, and if those liquids are highly volatile or contain volatile components, air emissions could result. Nevertheless, air emissions are rarely a problem in filtration applications.

In the cleaning or "backwashing" of granular media filters a small solids-contaminated wastewater stream is generated. If the solids are considered hazardous, this stream must be treated prior to disposal. Typically, when filters follow sedimentation basins, the backwash water is returned to the sedimentation basin where (after particles are removed) it will eventually be sent through the filter again. If this option is not available, the backwash water would have to be subjected to further treatment.

In rotary vacuum filters and filter presses used for sludge dewatering, the solids produced *are* the intended product. These applications also face a disposal problem associated with the liquid (filtrate) that has been removed from the sludge.

C. ECONOMIC ANALYSIS

Because of the widespread full-scale use of filtration, the operating parameters and economics are well defined and well documented. As with most processes, it is customary to identify two kinds of costs: capital investment, and total annual operating cost, the latter including certain capital-related components such as interest, depreciation, taxes, and insurance.

The capital investment of a given type of filter system is primarily a function of its characteristic size, and the characteristic size of most filters is expressed as the surface area of the filter medium. For processing a given type of waste, the size of the filter is determined by the rate at which material can be processed by the filter. This throughput rate is usually expressed as either the volumetric rate or mass rate of material processes per unit surface area of filter medium. In filtration applications in which the objective is to produce a purified liquid, the throughput rate is expressed in terms of volume of liquid filtered per unit time per unit surface area of filter medium. In filtration applications in which the objective is to produce a dewatered sludge, the throughput rate is expressed as the mass of solids filtered (dry weight basis) per unit time per unit surface area of filter medium.

Although filter throughput rates are highly dependent on both the type of waste treated and the specific filter design, the following throughput rates are generally encountered in most waste treatment applications.

- *Granular Media Filters* – Granular media filters used in water and wastewater treatment applications are usually operated at a throughput rate of 2-6 gallons per minute per sq ft of filter medium.
- *Vacuum Filters* – Vacuum filters used in sludge dewatering applications are usually operated at a throughput rate of 2-10 pounds per hour of solids (dry basis) processed per sq ft of filter medium.
- *Filter Presses* – Filter presses used in sludge dewatering applications are usually operated at a throughput rate of 0.2 – 2.0 pounds per hour of solids (dry basis) processed per sq ft of filter medium.

The major components of filter operating costs include:

- electrical power required to supply the pressure differential
- filter aid material (if used) such as diatomaceous earth, lime, and ferric chloride
- filter cloth, paper, or some other medium.
- operating and maintenance labor (vacuum filters and filter presses can sometimes be high labor and maintenance items).

To illustrate the economics of filtration as applied to a typical hazardous waste treatment application, an economic analysis has been performed on a vacuum filtration system used for the dewatering of a hazardous waste sludge.

The selected waste stream is a 36,000 gpd zinc hydroxide sludge (most likely the by-product of a large metal plating operation wastewater treatment system) containing zinc hydroxide at a 4% weight concentration (6 tons/day of zinc hydroxide).

An illustrative flow diagram of the treatment system is presented in Figure 4.

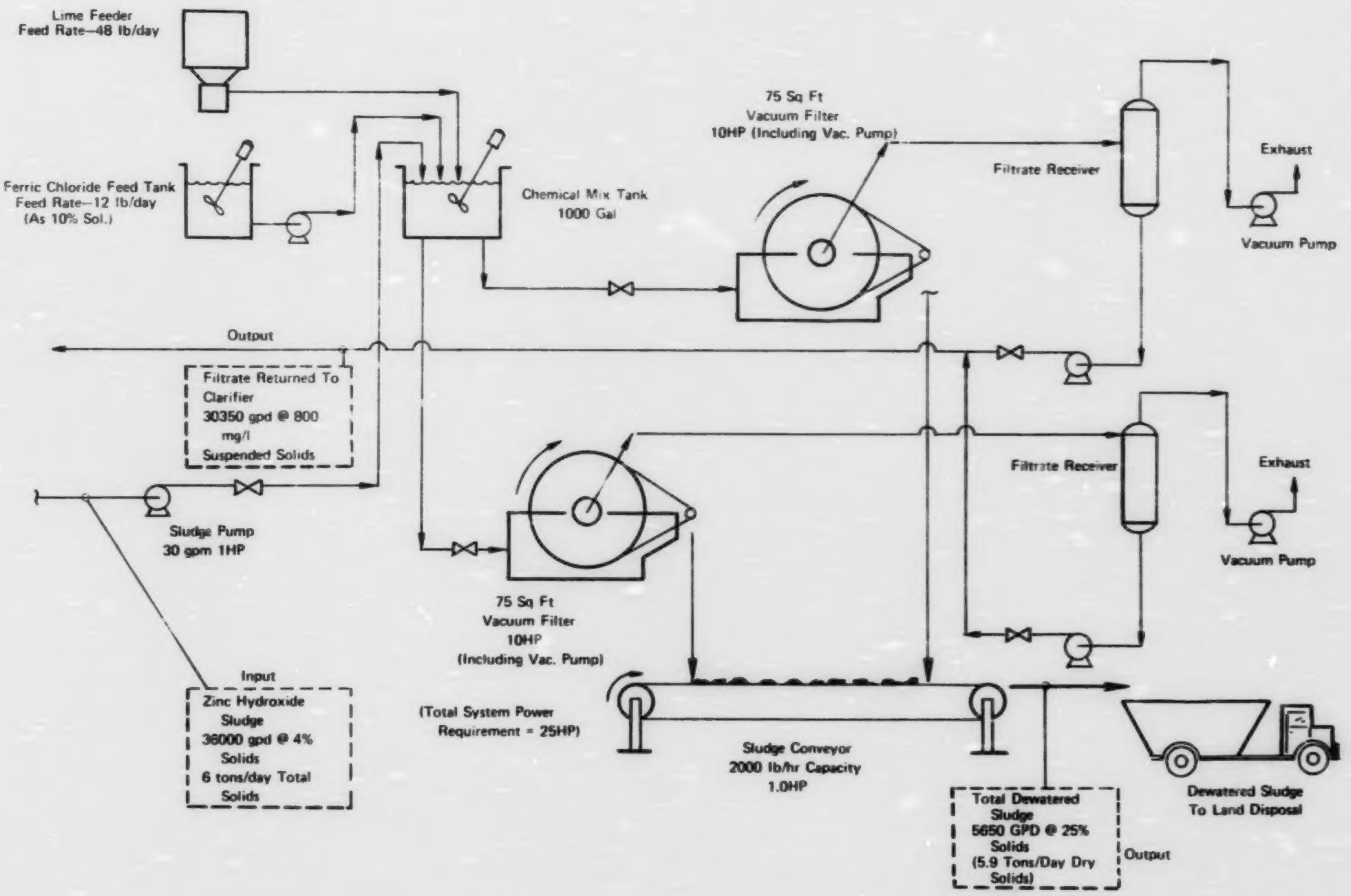

Lime Feeder
Feed Rate—48 lb/day
Ferric Chloride Feed Tank
Feed Rate—12 lb/day
(As 10% Sol.)
Chemical Mix Tank
1000 Gal
75 Sq Ft
Vacuum Filter
10HP (Including Vac. Pump)
Filtrate Receiver
Exhaust
Vacuum Pump
Output
Filtrate Returned To
Clarifier
30350 gpd @ 800
mg/l
Suspended Solids
Sludge Pump
30 gpm 1HP
75 Sq Ft
Vacuum Filter
10HP
(Including Vac. Pump)
Filtrate Receiver
Exhaust
Vacuum Pump
Input
Zinc Hydroxide
Sludge
36000 gpd @ 4%
Solids
6 tons/day Total
Solids
(Total System Power
Requirement = 25HP)
Sludge Conveyor
2000 lb/hr Capacity
1.0HP
Total Dewatered
Sludge
5650 GPD @ 25%
Solids
(5.9 Tons/Day Dry
Solids)
Output
Dewatered Sludge
To Land Disposal

FIGURE 4 VACUUM FILTRATION OF WASTE SLUDGE – ILLUSTRATIVE FLOW DIAGRAM
WASTE STREAM – ZINC HYDROXIDE SLUDGE

Referring to Figure 4, a brief description of the process scheme is as follows:

- Wet zinc hydroxide sludge (originating from a clarifier in which soluble zinc ions have been precipitated as zinc hydroxide) is first pumped to a chemical mix tank where lime and ferric chloride are added to the sludge in order to improve its dewatering characteristics.
- The sludge so conditioned is then fed by gravity to two vacuum filters.
- The vacuum filters dewater the sludge to a 25% solids concentration and deposit it onto a sludge conveyor where it is transported to a receiving station and then trucked to landfill.
- The filtered liquid (filtrate), which still contains an appreciable amount of suspended solids, is returned to the clarifier from which the sludge was originally drawn.

Cost estimates were developed for the process scheme depicted in Figure 4, and these are presented in Table 2. The total annual cost is divided into variable costs, which include all the components of the direct operating cost, and fixed costs, which include capital-related items such as capital recovery (interest and depreciation) and taxes and insurance.

For the illustrative system shown, the total annual cost is $80,800 per year, which on a unit cost basis translates to $38.50 per ton of dry solids processed. Such a cost is quite typical for this type of treatment system.

In considering treatment economics in a general sense, it is necessary to take into account economy-of-scale effects. The capital cost of most process equipment does not vary linearly with size, but rather, as the 0.5-0.8 power of size. Thus, tripling the size of a piece of process equipment will not triple the cost, but will only approximately double the cost. To illustrate this effect, two additional cost estimates were prepared – one for a treatment system one-third the size of that used in the example, and one for a system three times its size. These estimates are presented in Table 3.

As can be seen from Table 3, over a ninefold size range, the unit treatment cost for the illustrative system varies from $66.10/ton for the small system to $21.60/ton for the large system.

In most cases, sludge dewatering by use of either the vacuum filter or filter press result in unit treatment costs within the $20-$45/ton range.

TABLE 2

CAPITAL AND OPERATING COST ESTIMATES FOR ILLUSTRATIVE VACUUM FILTRATION SYSTEM APPLIED TO SLUDGE DEWATERING

Waste Stream: **Zinc Hydroxide Sludge**
36,000 gpd of 4% $Zn(OH)_2$ (by weight)
6 tons/day zinc hydroxide

Capital Investment – $200,000

	Annual Quantity	Cost Per Unit Quantity	Annual Cost ($/yr)
Variable Costs			
Operating Labor (including supervision plus overhead)	3,000 mh/yr	$12.00/hr	$36,000
Maintenance (Labor plus materials)	–	–	6,000
Chemicals			
• Hydrated Lime	2.1 tons/yr	$35.00/ton	75
• Ferric Chloride	8.4 tons/yr	$100/ton	840
Electrical Energy	156,700 kWh/yr	$0.02/kWh	3,100
Total Variable Cost			$44,200/yr
Fixed Costs			
Capital Recovery (10 yrs @ 10%)	–	–	32,600
Taxes and Insurance (@ 2% of capital investment)	–	–	4,000
Total Fixed Cost			$36,600/yr
Total Annual Cost	–	–	$80,800/yr
Unit Cost (cost per ton of dry solids processed)	–	–	$38.50/ton

Note: (1) Capital investment adjusted to January 1976 (Engineering News Record Construction Cost Index – 2305)
(2) Operating costs are based on a 24-hour per day, 350 day per year operating period
(3) Costs *do not* include sludge hauling and landfill costs

Source: Arthur D. Little, Inc., estimates.

TABLE 3

VACUUM FILTRATION COST ESTIMATES AS A FUNCTION OF SIZE

	Treatment System Size		
	12,000 gpd **(2 tpd solids)**	**36,000 gpd** **(6 tpd solids)**	**108,000 gpd** **(18 tpd solids)**
Capital Investment	$103,000	$200,000	$387,000
Variable Cost			
Labor	23,000	36,000	56,000
Maintenance	3,100	6,000	11,600
Chemicals			
• Hydrated Lime	25	75	225
• Ferric Chloride	280	840	2,500
Electrical Energy	1,000	3,100	9,300
Total Variable Cost	$27,400/yr	$44,200	$79,600
Fixed Cost			
Capital Recovery	16,800	32,600	63,100
Taxes and Insurance	2,100	4,000	7,700
Total Fixed Cost	$18,900/yr	$36,600/yr	$70,800/yr
Total Annual Cost	$46,300/yr	$80,800/yr	$150,400/yr
Unit Cost (cost per ton of dry solids processed)	$66.10/ton	$38.50/ton	$23.90/ton

Notes: All costs are for the waste stream and treatment process scheme depicted in Figure 4 of this study.

Source: Arthur D. Little, Inc., estimates.

- *Costs for Granular Media Filters* – In the purification of liquid wastewater streams by means of granular media filtration the total operating cost (including capital-related costs such as interest and depreciation) usually varies from $0.10-$0.50 per 1000 gallons of wastewater treated.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

As previously discussed, filtration is in widespread use in the treatment of industrial wastewater and waste sludges.

As a physical liquid/solid separation process, filtration shares potential applications with other liquid/solid separation processes, namely flocculation and/or sedimentation and centrifugation. The specific nature of a particular waste treatment problem dictates which liquid/solid separation process or combination of processes is most feasible. Summarized below are some of the general advantages and disadvantages of filtration as a waste treatment process:

Advantages

- *Demonstrated Operational Practicality* – Filtration has been in use for many years. The equipment is simple and commercially available, and the process is easy to operate and control.
- *Versatility* – Some form of filtration can potentially be applied to almost any free flowing liquid stream containing suspended solid particles.
- *Reasonable Cost* – While filtration is sometimes excluded from consideration for very high volume wastewater streams, the economics of filtration with regard to sludge dewatering applications are usually favorable enough to make filtration cost competitive with other sludge dewatering processes.
- *Reasonably Low Energy Consumption*
- *No Secondary Air Pollution Effects* – Filtration in itself does not produce any inherent secondary air pollution effects. Most filtration devices do expose liquid surfaces to the atmosphere (for at least part of the filtration cycle); and if the liquid should either be volatile or contain a volatile fraction, air pollution problems could result. Vacuum filtration of a volatile liquid can generate pollution in the gases discharged from the vacuum pumps or the steam ejector. In the dewatering of truly dangerous materials, filtration is at a definite disadvantage to centrifugation which can be operated in an almost totally enclosed fashion.
- *Easily Integrated with Other Treatment Steps* – Filtration often follows a sedimentation step in order to effect more complete removal of suspended solids. Also, filtration often precedes activated carbon adsorption in order to prevent plugging of the carbon columns.

- *Potential for Waste Recovery* – Filtration is a physical separation process, and therefore, does not destroy or seriously alter any of the components of the material treated. If either the liquid phase or the solid phase of a particular waste is recoverable, and if such recovery is advantageous; filtration will achieve the desired separation effectively, efficiently, and without damage to the recoverable component(s).

Disadvantages

- *Incomplete Removal for Sludge Dewatering Applications* – Both vacuum filtration and press filtration, while capable of effecting a desirable degree of sludge dewatering, are not usually capable of producing either a high purity liquid stream (unless heavy precoats are used, which tend to reduce the throughput) or a completely dry solids stream. Both the liquid product (filtrate) and the dewatered sludge will each contain a certain fraction of the original liquid and solid phases. If either the original liquid or the original solid is contaminated with hazardous materials, the product of filtration will also be contaminated to a certain degree.
- *Non-selective* – Being a purely physical separation process, filtration is incapable of separating chemical components from each other when they are present in the same phase.
- *Non-destructive* – Since it is a physical separation process, filtration is not capable of destroying or chemically altering hazardous materials. While this feature can sometimes be an advantage when recovery is possible, it is a disadvantage when recovery is not possible.
- *Production of a Liquid Waste Stream* – Granular media filters produce a waste backwash water stream. Rotary vacuum filters and filter presses produce a waste filtrate stream. If these streams contain soluble hazardous materials, a problem of disposal or further treatment will result.

Conclusions

Filtration is a fully developed process currently being used in a variety of full-scale material processing, wastewater treatment, and sludge dewatering applications. The operational parameters and economics of filtration are well defined and well documented. Filtration equipment is commercially available in a wide variety of sizes and configurations. Therefore, it is anticipated that filtration will continue to be a common process for treatment of industrial waste.

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3. Dr. John Ciancia, U.S. Environmental Protection Agency National Environmental Research Center, Edison, New Jersey

4. The Silresim Chemical Co., Lowell, Massachusetts

PRECIPITATION, FLOCCULATION, AND SEDIMENTATION

Prepared by

Edmund H. Dohnert

I. CONCLUSIONS AND RECOMMENDATIONS

Precipitation, flocculation, and sedimentation are well-developed processes currently being applied to the full-scale treatment of many industrial wastewaters containing particulates and/or soluble heavy metals. The operating parameters and economics associated with the application of precipitation, flocculation, and sedimentation to the treatment of specific industrial wastewater streams are well defined and well documented.

True research and development are usually unnecessary in determining whether a particular waste stream is amenable to precipitation, flocculation, and sedimentation. Past experience and simple laboratory treatability tests are usually all that is necessary in determining applicability.

We recommend that these processes be considered for treating liquid industrial wastes.

II. PROCESS DESCRIPTION

Precipitation, flocculation, and sedimentation are discussed together in a single report because in waste treatment they are most commonly used together, as consecutive treatments to the same stream. (See Figure 1.) Precipitation removes a substance in solution and transforms it into a second phase, often in the form of solid particles that may be small or even colloidal. Flocculation transforms small suspended particles into larger suspended particles so that they can be more easily removed. Sedimentation removes the suspended particles from the liquid.

A. PRECIPITATION

Precipitation, in the context of this analysis, is a physicochemical process whereby some or all of a substance in solution is transformed into a solid phase and thereby removed from solution. Precipitation involves an alteration of the chemical equilibrium relationships affecting the solubility of the component(s). This alteration can be achieved by a variety of means. Most precipitation reactions for industrial or waste treatment purposes are induced by one or a combination of the following steps:

1. Adding a substance that will react directly with the substance in solution to form a sparingly soluble compound.

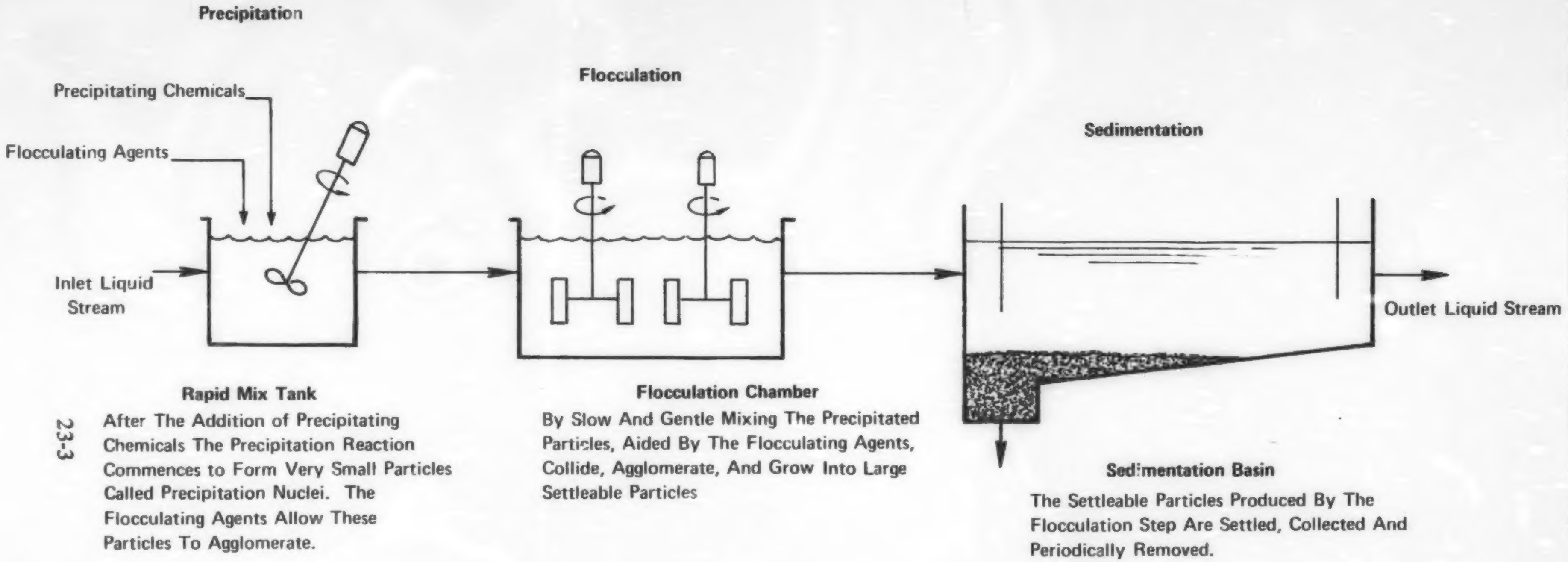
2. Adding a substance that will cause a shift in the solubility equilibrium to a point which no longer favors the continued solubility of the substance originally in solution.

3. Changing the temperature of a saturated or nearly saturated solution in the direction of decreased solubility; since solubility is a function of temperature, this change can cause ionic species to come out of solution and form a solid phase.

The most common precipitation reactions involve the removal of inorganic ionic species from various aqueous media.

Zinc chloride is highly soluble in water, as is sodium sulfide. Zinc sulfide, however, has an extremely low solubility in water. Thus, if an aqueous solution of zinc chloride is mixed with an aqueous solution of sodium sulfide, zinc ions and sulfide ions will rapidly combine to form solid zinc sulfide particles,

$$Zn^{2+} + 2\,Cl^- + 2Na^+ + S^{2-} \rightarrow \underset{\text{(solid)}}{\underset{\downarrow}{ZnS}} + 2Na^+ + 2Cl^-$$


Precipitation
Precipitating Chemicals
Flocculating Agents
Inlet Liquid Stream
Flocculation
Sedimentation
Outlet Liquid Stream

Rapid Mix Tank

After The Addition of Precipitating Chemicals The Precipitation Reaction Commences to Form Very Small Particles Called Precipitation Nuclei. The Flocculating Agents Allow These Particles To Agglomerate.

Flocculation Chamber

By Slow And Gentle Mixing The Precipitated Particles, Aided By The Flocculating Agents, Collide, Agglomerate, And Grow Into Large Settleable Particles

Sedimentation Basin

The Settleable Particles Produced By The Flocculation Step Are Settled, Collected And Periodically Removed.

FIGURE 1 REPRESENTATIVE CONFIGURATION EMPLOYING PRECIPITATION, FLOCCULATION, AND SEDIMENTATION

The mixing of the two solutions creates an unstable, highly supersaturated solution of zinc sulfide, which rapidly readjusts itself toward equilibrium by the creation of a solid zinc sulfide phase. The resultant liquid/solid mixture is essentially a suspension of solid ZnS in a saturated but necessarily very dilute solution of zinc sulfide. In this [illegible], as in most precipitation reactions, the governing equilibrium relationship is the solubility product (K_{sp}) of the substance that eventually forms the solid phase. The solubility product is basically an expression of the maximum concentration of ionic species that will be in equilibrium with the respective solid phase. For this example, the solubility equilibrium expression would be

$$[Zn^{2+}]\ [S^{2-}] = K_{sp}$$

If solid zinc sulfide is contacted with water, dissolution will occur, putting zinc and sulfide ions into solution until the product of the ionic zinc concentration and the ionic sulfide concentration is equal to the solubility product. Both precipitation and dissolution involve an approach toward the solubility equilibrium or "saturation point." In dissolution, equilibrium is approached from a state below the saturation point; in precipitation, equilibrium is approached from a state above the saturation point. The equilibrium point itself can be a function of a number of variables, e.g., temperature, and ionic strength, and is often influenced by the presence of other dissolved species, which can enter into additional completion and/or solubility relationships.

In many precipitation and dissolution reactions, pH is a master variable affecting the equilibrium concentration of ionic species. This is particularly true where the respective solid phase is a hydroxide or carbonate compound. Since the hydroxide concentration of a solution is pH-dependent (by definition), many precipitation reactions can be induced by varying the pH of the original solution. For example, if solid ferrous hydroxide is contacted with water, the following dissolution reaction will occur (but only slightly),

$$Fe\,(OH)_{2(s)} = Fe^{2+} + 2OH^-$$

and the equilibrium expression can be written as,

$$[Fe^{2+}]\ [OH^-]^2 = K_{sp}$$

Thus, solid ferrous hydroxide will continue to dissolve until the product of the ferrous ion concentration and the square of the hydroxide ion concentration equals the respective solubility product. If a strong acid is added to the equilibrated solution (thus lowering pH), the hydroxide ions will be neutralized and the solution will no longer be in equilibrium with the solid phase. Instead, it will now be below the saturation point. Equilibrium is again attained as more ferrous ions go into solution. Thus, as the pH is lowered, more and more ferrous ions will go into solution.

Approaching equilibrium from the reverse direction, if a strong caustic such as sodium hydroxide is added to an aqueous (and necessarily slightly acidic) solution of ferrous ions, the solubility product of $Fe(OH)_2$ will be exceeded, thus causing the creation of a solid ferrous hydroxide phase as the solution returns to equilibrium.

In certain industrial applications, precipitation of a desired product material is induced by chilling a saturated solution. Since most salts are less soluble at lower temperatures (calcium carbonate and calcium sulfate being two notable exceptions), chilling a saturated solution of such salts causes the equilibrium to be disturbed. The equilibrium is readjusted by the removal of ions from solution and the creation of a solid phase. This technique has very limited applications for waste treatment purposes, mainly due to the fact that solubility of most slightly soluble compounds used in precipitation schemes is a weak function of temperature, and therefore, very large differences in concentration cannot usually be achieved.

Physically, most precipitation reactions are carried out by adding the appropriate chemicals to the solution and mixing thoroughly. Although most precipitation reactions take place extremely rapidly, a moderate amount of time is usually required to allow the chemicals to be dispersed throughout the solution. Characteristically, the solid particles, when first formed, are very small. Depending on the nature of the chemical system involved and the types of further treatment applied, the solid particles can remain as submicroscopic precipitation nuclei, or very small colloidal particles; or they can grow into larger particles. The particles may either be crystalline or amorphous.

It is important to recognize that the term precipitation, as strictly defined, refers only to the conversion of dissolved substances into insoluble ones in order to facilitate their subsequent removal from the liquid phase. Precipitation, per se, does not refer to any of the liquid-solid separation processes that are required to remove the precipitated solid particles from the original volume of liquid. In order to effect the removal of precipitated particles from a volume of liquid, it is very often necessary to apply additional process steps, and these often involve flocculation, sedimentation, and/or some control which will determine the final particle size – and produce an easily separable solid (or crystal).

B. FLOCCULATION

Historically, the terms "flocculation" and "coagulation" have been used rather indiscriminately and interchangeably to describe the process by which small, unsettleable particles suspended in a liquid medium are made to agglomerate into larger, more settleable particles. Distinctions between the two terms frequently appear in the water and waste treatment literature; however, the definitions used are often conflicting (Refs. 1,2), and the result is that there are really no precise and universally accepted technical definitions of these terms. For the purpose of this study, the term "flocculation" shall be defined so as to encompass all of the mechanisms by which the above-mentioned suspended particles agglomerate into larger particles. As a general term used in this study, no distinction will be made between coagulation and flocculation.

Many liquid-solid separation processes, such as sedimentation, are based on the use of gravitational and/or inertial forces to remove solid particles from a liquid. It is generally true that the larger the particle size, the easier will be the removal of the particle from the liquid.

There are a variety of forces acting on particles suspended in a liquid. There are gravitational and inertial forces which are related to the mass of the particles; and there are also electrostatic and interionic forces which are surface-related. Thus, in the regime of very small particles the surface-related electrostatic and interionic forces tend to predominate; while in the regime of larger particles, the gravitational and inertial forces predominate. The surface-related electrostatic and interionic forces typically tend to repel particles away from each other. These forces are often the reason why very fine particles suspended in a liquid can sometimes remain suspended indefinitely. In the size regime of the small particles, the forces repelling the particles from each other are often greater than the gravitational forces tending to make the particles settle. The purpose of what we describe as flocculation is to overcome the above repulsive forces and to cause small particles to agglomerate into larger particles, so that gravitational and inertial forces will predominate and effect the settling of the particles.

In flocculation, as defined, there are a variety of mechanisms involved in the process whereby small particles are made to form larger particles. Most of these mechanisms involve surface chemistry and particle charge phenomena. In simple terms, these various phenomena can be grouped into two sequential mechanisms.

1. Chemically induced destabilization of the repulsive surface-related forces, thus allowing particles to stick together when contact between particles is made.

2. Chemical bridging and physical enmeshment between the now non-repelling particles, thus allowing for the formation of large particles.

Typically, chemicals used to cause flocculation include alum, lime, various iron salts (ferric chloride, ferrous sulfate). Relatively recently, organic flocculating agents, often referred to as "polyelectrolytes" have come into widespread use. These materials generally consist of long-chain water-soluble polymers such as polyacrylamides. They are used either in conjunction with the inorganic flocculants such as alum or as the primary flocculating agent itself.

The inorganic flocculants, such as alum, lime, or iron salts, make use of precipitation reactions. Alum (hydrated aluminum sulfate) is typically added to aqueous waste streams as a solution. Upon mixing, the slightly higher pH of the water causes the alum to hydrolize and form fluffy, gelatinous precipitates of aluminum hydroxide. These precipitates, partially due to their large surface area, act to enmesh small particles and thereby create larger particles. Lime and iron salts, as well as alum, are used as flocculants primarily because of this tendency to form large fluffy precipitates or "floc" particles. Many precipitation reactions, such as the precipitation of metals from solution by the addition of sulfide ions, do not readily form floc particles, but rather precipitate as very fine and relatively stable colloidal particles. In such cases, flocculating agents such as alum and/or polyelectrolytes must be added to cause flocculation of the metal sulfide precipitates.

In actual practice, the flocculation process entails the following steps:

1. Addition of the flocculating agent to the liquid.
2. Rapid mixing to disperse the flocculating agent throughout the liquid.
3. Slow and gentle mixing to allow for contact between small particles and agglomeration into larger particles.

In the flocculation process it is essential that the slow mixing step is very gentle and is given sufficient time, as newly agglomerated particles are quite fragile and can be broken apart by shear forces during mixing.

Once suspended particles have been flocculated into larger particles, they can usually be removed from the liquid by sedimentation, provided, of course, that a sufficient density difference exists between the suspended matter and the liquid. An illustrative flocculation process is shown and described in Figure 2.

C. SEDIMENTATION

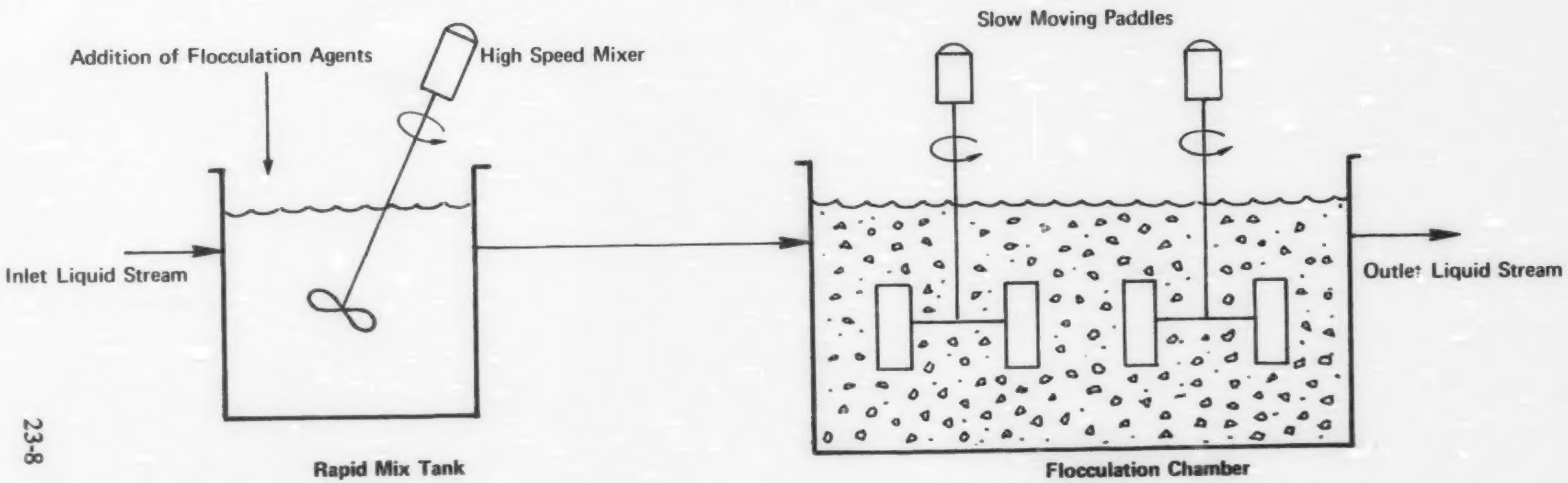
Sedimentation is a purely physical process whereby particles suspended in a liquid are made to settle by means of gravitational and inertial forces acting on both the particles suspended in the liquid and the liquid itself. Basically, particles are made to settle out of a liquid by creating conditions in which the gravitational and inertial forces acting on the particle in the desired direction of settling are greater in magnitude than the various forces (drag forces, inertial forces) acting in the opposite direction. This force differential causes the particles to travel in the desired direction.

The fundamental elements of most sedimentation processes are:

1. A basin or container of sufficient size to maintain the liquid to be treated in a relatively quiescent state for a specified period of time.

2. A means of directing the liquid to be treated into the above basin in a manner which is conducive to settling.

3. A means of physically removing the settled particles from the liquid (or the liquid from the settled particles, whichever the case may be).



Addition of Flocculation Agents
High Speed Mixer
Slow Moving Paddles
Inlet Liquid Stream
Outlet Liquid Stream
Rapid Mix Tank
Flocculation Chamber

Rapid Mix Tank

Flocculating Agents, e.g., Alum, Ferric Sulfate, Polyclectrolytes, Are Intimately Mixed With The Liquid To Cause a Destabilization of Inter-Particle Repelling Forces.

Typical Residence Time 1 To 5 Minutes

Flocculation Chamber

By Slow And Gentle Mixing Suspended Particles Collide With One Another, And Agglomerate Into Larger Particles.

Typical Residence Time 10 To 30 Minutes

FIGURE 2 ILLUSTRATIVE FLOCCULATION PROCESS

Sedimentation can be carried out as either a batch or a continuous process. Continuous processes are by far the most common, particularly when large volumes of liquid are to be treated.

In a continuous process there is an inherent liquid velocity as the liquid flows through the basin or container. Due to this velocity, there is a drag force exerted by the liquid on the particle in the direction of the liquid flow, resulting in a tendency for the particle to travel in the direction of the flowing liquid. There is also a gravitational force acting on the particle in a downward direction. For this gravitational force to result in a downward movement of the particle, the particle's density must be greater than that of the liquid it is suspended in. (If its density is less, the particle will tend to float rather than settle.) The rate of settling will depend on the particle size, particle density, liquid density and liquid viscosity. For settling to take place in a continuous system, the resultant force vector acting on the particle must be such that the trajectory of the particle is in a direction that will cause the particle to be retained within the container as the liquid flows through the container. (In certain types of sedimentation equipment, inertial forces supplement gravitational forces by means of causing the liquid stream to abruptly change direction.)

Depending on the specific process configuration, the settled particles are either removed from the bulk of the liquid, or the liquid is separated from the settled particles by decantation. Either way, the end result and single purpose of sedimentation is liquid/solid separation. The fraction of liquid containing the settled particles is commonly referred to as "sludge."

Sedimentation can be carried out in rudimentary settling ponds, conventional settling basins, or in more advanced clarifiers which are often equipped with built-in flocculation zones and tube-like devices that enhance settling.

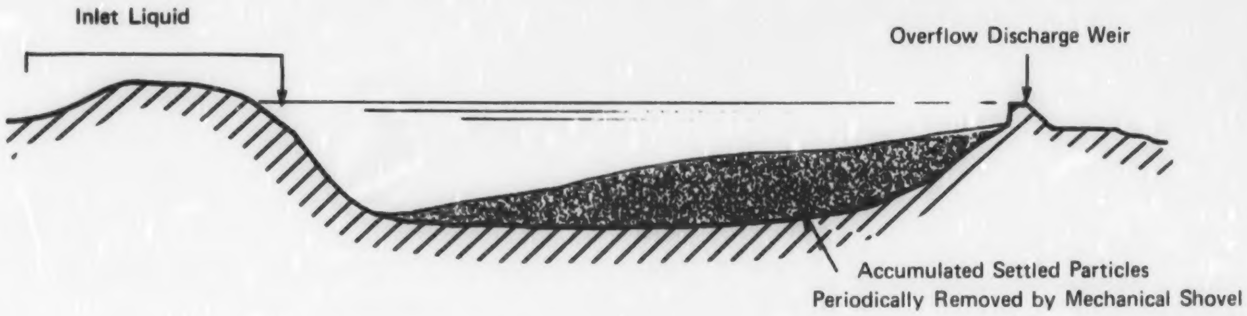
In settling ponds, the liquid is merely decanted as the particles accumulate on the bottom of the pond and eventually fill it. Often the pond is periodically emptied of particles by mechanical shovels, draglines, or siphons. Sedimentation basins and clarifiers are more sophisticated and usually employ a built-in solids collection and removal device such as a sludge scraper and draw-off mechanism. Sedimentation basins tend to be rectangular in configuration, usually employ a belt-like collection mechanism, and tend to be used more for the removal of truly settleable particles from a liquid.

Clarifiers are generally circular, and are usually the type of equipment used in applications that involve precipitation and flocculation in addition to sedimentation. Very often all three processes take place within the same piece of equipment, since many clarifiers are equipped with separate zones for chemical mixing and precipitation, flocculation, and of course, settling. Certain clarifiers are equipped with low lift turbines which mix a portion of the previously settled precipitates with the incoming feed, as this practice has been shown to enhance certain precipitation reactions and promote favorable particle growth. (This type of clarifier is often used in water softening applications involving the precipitation of calcium as calcium carbonate.)

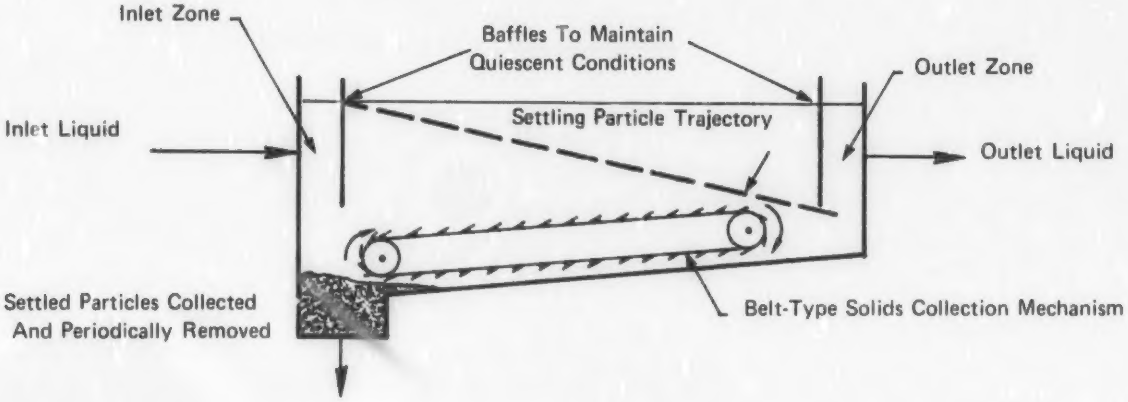
In recent years a number of commercial tube-like devices intended for the improvement of settling characteristics have been used in numerous applications. These devices, commonly called "tube-settlers," typically consist of thin-walled rectangular plastic tubes (several inches square and several feet long) that are arranged in an inclined honeycomb configuration in the settling zone of a clarifier. By reducing turbulence and by causing particles to impinge on the tube walls, a greater flowrate can be put through the clarifier while still maintaining the original clarifier surface area.

There are many variations of the sedimentation process, encompassing a wide variety of commerically available equipment. Some of the more representative types are shown in Figure 3.

Settling Pond


Inlet Liquid
Overflow Discharge Weir
Accumulated Settled Particles
Periodically Removed by Mechanical Shovel

Sedimentation Basin


Inlet Zone
Baffles To Maintain
Quiescent Conditions
Outlet Zone
Inlet Liquid
Settling Particle Trajectory
Outlet Liquid
Settled Particles Collected
And Periodically Removed
Belt-Type Solids Collection Mechanism

Circular Clarifier

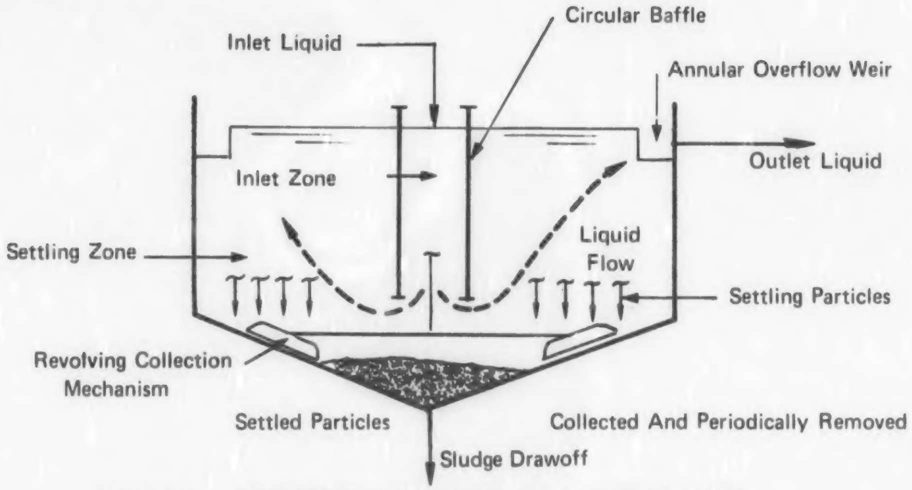

Circular Baffle
Inlet Liquid
Annular Overflow Weir
Outlet Liquid
Inlet Zone
Settling Zone
Liquid
Flow
Settling Particles
Revolving Collection
Mechanism
Settled Particles
Collected And Periodically Removed
Sludge Drawoff

FIGURE 3 REPRESENTATIVE TYPES OF SEDIMENTATION

III. APPLICATIONS TO DATE

Precipitation, flocculation, and sedimentation have been in use since the 19th Century for a wide variety of industrial applications. Today, the processes are used in the manufacture of chemicals, and in the treatment of industrial water supplies and industrial wastewater. Wherever it is necessary to remove precipitable soluble substances and/or suspended particles from liquid streams, the processes may be applied. While the vast majority of applications involve the treatment of aqueous streams, the processes can also be applied to non-aqueous liquids.

A. PRINCIPAL CURRENT APPLICATIONS

1. Industrial Manufacturing Applications

Some typical examples of the use of precipitation, flocculation, and sedimentation in industrial manufacturing applications are listed below.

a. Chlorine Manufacture

Prior to electrolysis it is necessary to remove calcium and magnesium salts from the concentrated brine. These salts are removed by precipitation, flocculation, and sedimentation. Typically, lime and soda ash are used to cause the soluble calcium salts to precipitate as calcium carbonate and the magnesium to precipitate as magnesium hydroxide. While calcium carbonate and magnesium hydroxide precipitate quite readily, it is usually necessary to provide a flocculation step (often utilizing polyelectrolyte flocculating agents) to produce particles large enough for effective removal by sedimentation (Ref. 3).

b. Magnesium Production from Sea Water

Magnesium, present in sea water as a chloride, is removed from the sea water by precipitation, flocculation, and sedimentation, using lime to form insoluble solid particles of magnesium hydroxide (Ref. 3).

c. Manufacture of Sugar

The raw juices from crushed sugar cane are treated with lime to coagulate (flocculate) colloidal matter, and to precipitate some of the impurities (Ref. 3).

d. Manufacture of Paper

Certain papers are coated with titanium dioxide and clays by coagulating (flocculating) colloidal particles of these materials onto the surface of the paper, using alum as the flocculating agent (Ref. 3).

There are many more actual process applications of precipitation, flocculation, and sedimentation throughout industry.

2. Industrial Water Treatment Applications

Industrial manufacturing processes often have strict specifications on process water quality that require the removal of both suspended particles and certain soluble substances from the water. Typically, it is necessary to remove calcium and magnesium compounds from water, as these are prone to form scale deposits within piping systems of the process equipment. The most common method of calcium and magnesium removal is precipitation by lime and/or soda ash, followed by the subsequent removal of the precipitated particles by flocculation and sedimentation. In a like manner, suspended solids in the water are often removed from the water by flocculation and sedimentation, using alum and polyelectrolytes.

3. Industrial Wastewater Treatment Applications

With regard to the objectives of the study, the most significant industrial application of precipitation, flocculation, and sedimentation is the treatment of industrial wastewater. Practically every industry that discharges a process wastewater stream contaminated with suspended and/or precipitable pollutants employs some form of precipitation/flocculation and/or sedimentation.

The processes of precipitation, flocculation, and sedimentation are finding widespread application in the treatment of wastewater streams containing soluble heavy metals and colloidal hazardous substances. A summary of general wastewater treatment applications in a number of major industries is presented below.

a. Iron and Steel Industry

Wastewater streams from the iron and steel industry are characterized by a very high concentration of settleable suspended particles and a relatively low concentration of dissolved heavy metals, such as ferric iron, zinc, lead, chromium, and manganese. Sedimentation is currently in widespread use for the removal of suspended solids; and precipitation (usually with lime and alum) is used to remove the heavy metals (Ref. 4).

b. Aluminum Industry

Wastewater streams from the aluminum industry contain high concentrations of soluble fluoride salts. The commonly used treatment process entails precipitation as calcium fluoride (with lime), flocculation, and sedimentation to remove the fluoride as solid particles (Ref. 5).

c. Copper Industry

Wastewater streams from copper smelting and refining contain a variety of soluble and colloidal heavy metals (arsenic, cadmium, copper, iron, lead, mercury) which can be removed, to varying degrees of effectiveness, by precipitation, flocculation, and sedimentation using either lime or sodium sulfide (Ref. 6).

d. Metal Finishing Industry

Soluble salts of copper, nickel, cadmium, and chromium are removed from wastewater streams by precipitation, as hydrated oxides using lime, followed by flocculation, and sedimentation (Refs. 7,8). Any chromium usually present as chromate or dichromate must first be reduced to the trivalent state so that the precipitation process will be effective. Attempts have been made to recover some of these metals from the sludges formed, but in most cases it is not economically feasible (Ref. 9).

e. Inorganic Chemicals Industry

Many manufacturing processes within the inorganic chemicals industry produce wastewaters that contain suspended solids and soluble heavy metals. Examples are found in the manufacture of titanium dioxide and chromium pigments. Precipitation, flocculation, and sedimentation are used to treat many of these wastewaters (Ref. 10).

f. Pesticides

In the manufacture of certain pesticides, i.e., DDT and Toxaphene, sedimentation (with flocculation) is under consideration as a preliminary treatment step within a contemplated wastewater treatment scheme involving other steps (Ref. 11).

g. In Conjunction with Biological Treatment

Many industries, e.g., textiles, organic chemicals, pulp and paper, petroleum refining, and food processing, use some form of biological treatment for the treatment of wastewater. Very often, some form of sedimentation (sometimes with flocculation) is used after the biological treatment step to effect additional removal of pollutants and to remove excess bio-mass.

h. Sludge Thickening

As previously described, in the sedimentation process, the solids that are removed from the original liquid are in the form of a two-phase liquid/solid mixture called a "sludge." Whether a pond settling basin or clarifier is used for the sedimentation process, the sludge, as it is drawn off, is usually rather thin in consistency (typically 2%-15% solids by weight). In many cases the sludge must be subjected to a number of concentrating steps prior to final disposal. The purpose of the concentrating (dewatering) steps is to remove water from the sludge, thereby decreasing the volume of solids destined for final disposal. Often, the first step used in a sludge dewatering process is simply a better sedimentation process commonly referred to as "sludge thickening" or "gravity thickening." In the gravity thickening of sludges, the sludge is sent to a type of clarifier in which the already settled solid particles are allowed to further settle and compact. Typically, the supernatant liquid is returned to the main clarifier that performs the initial liquid/solid separation, while the "thickened" sludge is drawn off and either disposed of or sent to further dewatering steps, such as vacuum filtration or centrifugation.

4. Hazardous Waste Treatment Applications

As discussed in the previous section, precipitation, flocculation, and sedimentation are currently in widespread use throughout many industries for the treatment of process wastewater. With regard to wastewater streams that could be categorized as "hazardous," the most common existing application is the removal of toxic heavy metals from wastewater by lime treatment. Heavy metals commonly encountered in wastewater streams and generally considered quite harmful from an environmental point of view include arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc.

The following are specific examples of the use of precipitation, flocculation, and sedimentation.

a. Arsenic

Soluble arsenic has been removed from wastewater by means of precipitation, flocculation, and sedimentation using either lime (Ref. 12) (full-scale), ferric chloride (pilot plant) (Ref. 13), or sulfide salts (pilot plant) (Ref. 14).

b. Cadmium

Cadmium is currently being removed from wastewater in full-scale treatment facilities, by means of precipitation, flocculation, and sedimentation using lime (Refs. 15,16).

c. Chromium

Chromium is currently being removed from wastewater, in full-scale treatment facilities, by means of precipitation, flocculation, and sedimentation using lime. It is necessary to reduce hexavalent chromium to trivalent chromium before effective precipitation can be carried out. Sulfide precipitation has also been successful in removing chromium although it is not as commonly used as lime precipitation (Ref. 8).

d. Copper

Copper is currently being removed from wastewater, in full-scale treatment facilities, by means of precipitation, flocculation, and sedimentation using lime (Refs. 8,14).

e. Lead

Lead is currently being removed from wastewater, in full-scale treatment facilities, by means of precipitation, flocculation, and sedimentation using lime (Ref. 17).

f. Mercury

Mercury has been successfully removed from wastewater, in pilot-scale facilities, by means of precipitation, flocculation, and sedimentation using sulfide salts in conjunction with alum, lime, and coagulant aids (Refs. 17-19).

g. Nickel

Nickel is currently being removed from wastewater in full-scale treatment facilities, by means of precipitation, flocculation, and sedimentation using lime (Ref. 8).

In addition to applications involving specific point source discharges of industrial wastewater, precipitation, flocculation, and sedimentation are also employed by a number of contract waste disposal firms that accept liquid wastes containing heavy metals. Typically, these applications involve the treatment of chromium- or copper-containing liquid wastes of very low volume (sometimes batch operations) and relatively high concentration.

h. Dye Wastes

Many dye manufacture and/or preparation wastes contain colloidal dye material suspended in an aqueous medium. At least one contract disposal firm removes the suspended dye material from the aqueous stream by means of a batch precipitation, flocculation, and sedimentation process using alum and lime (Ref. 22).

i. Pulp and Paper and Textile Mill Color Removal

Wastewater effluents from certain pulp and paper mills and textile mills contain organic colloidals which are highly colored and are therefore often objectionable from an aesthetic point of view. Several pulp and paper mills now employ precipitation, flocculation, and sedimentation for the removal of such particles. Depending on the process, lime or alum can be used to perform the precipitation/flocculation. Similar processes can be applied to textile mill effluents (Ref. 23).

B. POTENTIAL APPLICATIONS FOR HAZARDOUS WASTE TREATMENT

Wherever a precipitable substance or suspended particles are present in a liquid stream, it is possible to apply precipitation, flocculation, and sedimentation. Although most existing applications involve the precipitation and subsequent removal of soluble heavy metals from wastewater streams under alkaline conditions, other potential applications exist. Due to the nature of the processes, the only fundamental limitation, in terms of direct applications, is that the hazardous waste to be removed must be contained in a liquid stream.

Potential applications of precipitation, flocculation, and sedimentation to various forms of hazardous wastes are discussed below.

1. Aqueous

As suggested in the preceding sections of this report, the major potential application of precipitation, flocculation, and sedimentation is likely to remain the treatment of aqueous waste streams.

2. Non-Aqueous Liquid

Precipitation and sedimentation can be applied to certain non-aqueous liquids. Likely potential applications would include the removal of precipitable substances or suspended particles from waste organic solvents. The degree of applicability would greatly depend on the viscosity of the solvent and the nature of the contaminants present. For precipitation, flocculation, and sedimentation to generally be effective, the viscosity of the liquid must not be overly high. It is not very likely that the processes can be applied very successfully to heavy, barely flowing liquid organic polymeric wastes. While it may be possible to induce certain precipitation reactions within such materials, flocculation and sedimentation would be greatly inhibited.

3. Slurries and Sludges

As previously mentioned, a form of sedimentation, i.e., "gravity thickening," is used to concentrate sludges and slurries. Since many hazardous materials are in the form of slurries and sludges, sedimentation can be applied to these wastes to reduce their volume and thereby alleviate at least a part of the overall disposal problem. Generally, after sedimentation, the hazardous waste will not be changed in form or chemical composition; it will only be more concentrated.

If the liquid fraction of the sludge or slurry contains soluble pollutants such as heavy metals, the addition of precipitating and flocculating agents during the sedimentation (thickening) process can cause these substances to leave the liquid fraction and report to the settled solids. In this case, the pollutants can be concentrated into a smaller volume. Generally (and there are exceptions) heavy metals in the form of solid precipitated particles such as metal sulfides, hydroxides, or carbonates are less environmentally harmful than their respective ions in solution. It is well to point out, though, that under many natural environmental conditions the precipitated metals can be dissolved back into ions in solution. For example, insoluble metal sulfides over long time periods tend to undergo biologically mediated oxidation to highly soluble metal sulfates. This phenomenon is well-known and is in fact one of the causes of acid mine drainage.

If slurries or sludges contain hazardous materials such as metals not in solution but rather as solid particles intimately mixed throughout the sludge, precipitation, flocculation, and sedimentation, in themselves, will not be able to remove these substances from the body of the sludge. However, if the sludge can first be subjected to a step in which the metals are selectively leached out of the body of the sludge (e.g., with acids, ammonium carbonate solutions, or organic solvents), the liquid containing the dissolved metals can then be treated separately via precipitation, flocculation, and sedimentation to remove the metals. The feasibility of this concept has been studied both by ADL and by others (Ref. 21). It is not generally used at present due to a variety of both theoretical and practical drawbacks.

4. Tars

While there may be exceptions, tars, because of their highly viscous nature, do not lend themselves to treatment by precipitation, flocculation, and sedimentation.

5. Solids, Dry Powders, and Gases

Because of the fundamental nature of the processes, precipitation, flocculation, and sedimentation are clearly not applicable to the treatment of hazardous wastes that are in the form of solids, dry powders, or gases.

Table 1 summarizes the potential applicability of precipitation, flocculation, and sedimentation to treat various forms of hazardous wastes. The potential applicability is divided into two groups: (1) removal of soluble species via precipitation, flocculation, and sedimentation and (2) liquid/solid separation via flocculation and/or sedimentation.

TABLE 1

POTENTIAL APPLICABILITY OF PRECIPITATION, FLOCCULATION, AND SEDIMENTATION TO VARIOUS FORMS OF HAZARDOUS WASTES

I. Removal of Soluble Species via Precipitation, Flocculation, and Sedimentation

Waste Form	Potential Applicability
Aqueous	High
Non-Aqueous Liquid	Moderate
Slurries	Low-Moderate
Sludges	Low
Tars	Not Applicable
Solids	Not Applicable
Dry Powders	Not Applicable
Gases	Not Applicable

II. Liquid/Solid Separation via Flocculation and/or Sedimentation

Waste Form	Potential Applicability
Aqueous	High
Non-Aqueous Liquid	Moderate
Slurries	Moderate
Sludges	Moderate
Tars	Not Applicable
Solids	Not Applicable
Dry Powders	Not Applicable
Gases	Not Applicable

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

The processes of precipitation, flocculation, and sedimentation are very low energy consumers compared with many other processes used to treat hazardous wastes. All of the energy consumed is mechanical energy required for pumping the liquid to and from the basins, mixing the chemicals with the liquid, and collecting the settled sludge. For a given size, clarifiers with solids recirculation will have a slightly higher power requirement than conventional settling basins. Usually, the energy required is a function of the volume of liquid treated rather than the composition of the liquid, and for a given type of equipment the power required is reasonably linearly proportioned to the volume treated. As an example, the total power required for a complete system employing precipitation, flocculation, and sedimentation, that is capable of treating 10 million gallons per day of wastewater, will typically be 40-200 HP, depending on the specific design. (This includes all pumping, mixing, and sludge-handling power requirements.)

B. ENVIRONMENTAL CONSIDERATIONS

Since the precipitation, flocculation, and sedimentation process is basically a liquid-solid separation process, it is inherent in the nature of the process that two output streams will result – a high-volume purified liquid stream and a low-volume slurried solids stream. As a rule, there are no air emissions from the process. The processes do employ equipment that exposes large open surfaces of liquid to the atmosphere; and if that liquid is other than water and is highly volatile or contains highly volatile components, air emissions could result. However, air emissions are seldom a problem for most applications involving the treatment of aqueous wastes.

The processes do produce solid wastes simply because it is the function of the process to separate solids from a liquid stream. Inherently, the solids from the process are contained within a liquid fraction which will be disposed of with the actual solids. This liquid slurry or sludge is usually treated to reduce its volume by some means of dewatering, but in most cases the liquid component is never completely eliminated. If the liquid component of the sludge contains hazardous materials, then the entire sludge volume will be contaminated with those materials.

The processes of precipitation, flocculation, and sedimentation pose a minimal safety and health hazard. The entire system is operated at near-ambient conditions, and there is, therefore, none of the danger of high pressure/high temperature operation. While chemicals such as alum and sodium hydroxide are powerful skin irritants, it is quite easy to handle these materials in a routinely safe manner.

C. ECONOMIC ANALYSIS

Since the processes of precipitation, flocculation, and sedimentation have been in full-scale operation for many decades, the operating parameters and economics are well defined. In applying the processes to potential waste streams, standardized tests are usually applied to determine:

1. The degree to which a substance will precipitate, along with the reaction time and the required chemical dosages.

2. The type of flocculating agents that must be used and the time required for flocculation.

3. The settling rate of the flocculated material.

The chemical dosages will, to a large degree, determine the direct operating costs, while the settling rate greatly determines the physical size of the equipment that must be used, and thus the capital investment.

In precipitation, flocculation, and sedimentation applications, the primary design parameter that sets the size of the settling basin or clarifier used is the so-called "overflow rate" expressed as hydraulic flowrate per unit of horizontal surface area (gpd/sq ft). The overflow rate is basically an expression of the gross velocity of the liquid passing through the settling device. At a given overflow rate, particles of a certain size and density will be capable of settling against the opposing flow of the liquid stream.

In most water and wastewater treatment applications, the overflow rate usually varies from 100 gpd/sq ft to 1500 gpd/sq ft. Heavy particles can be settled using high overflow rates, while light, small, poorly flocculated precipitates require lower overflow rates. Most typical overflow rates are in the 300-800 gpd/sq ft range.

To illustrate the economics of precipitation, flocculation, and sedimentation, we have performed an economic analysis on the use of these processes to treat a representative wastewater stream.

The selected wastewater stream is a 410,000 gpd wastewater stream from an automotive plating operation. The stream contains 113 mg/l of zinc and initially 204 mg/l of cyanide. In the generally accepted treatment of this waste stream, the wastewater is first subjected to cyanide destruction prior to zinc precipitation. In our example, the processes of precipitation, flocculation, and sedimentation are applied after the cyanide destruction step. The cyanide destruction step (most likely alkaline chlorination) is therefore not part of this economic analysis, and, for purposes of this discussion, we shall consider that only the zinc is present. An illustrative flow diagram of the treatment system designed to remove most of this zinc contamination from the waste stream is presented in Figure 4.

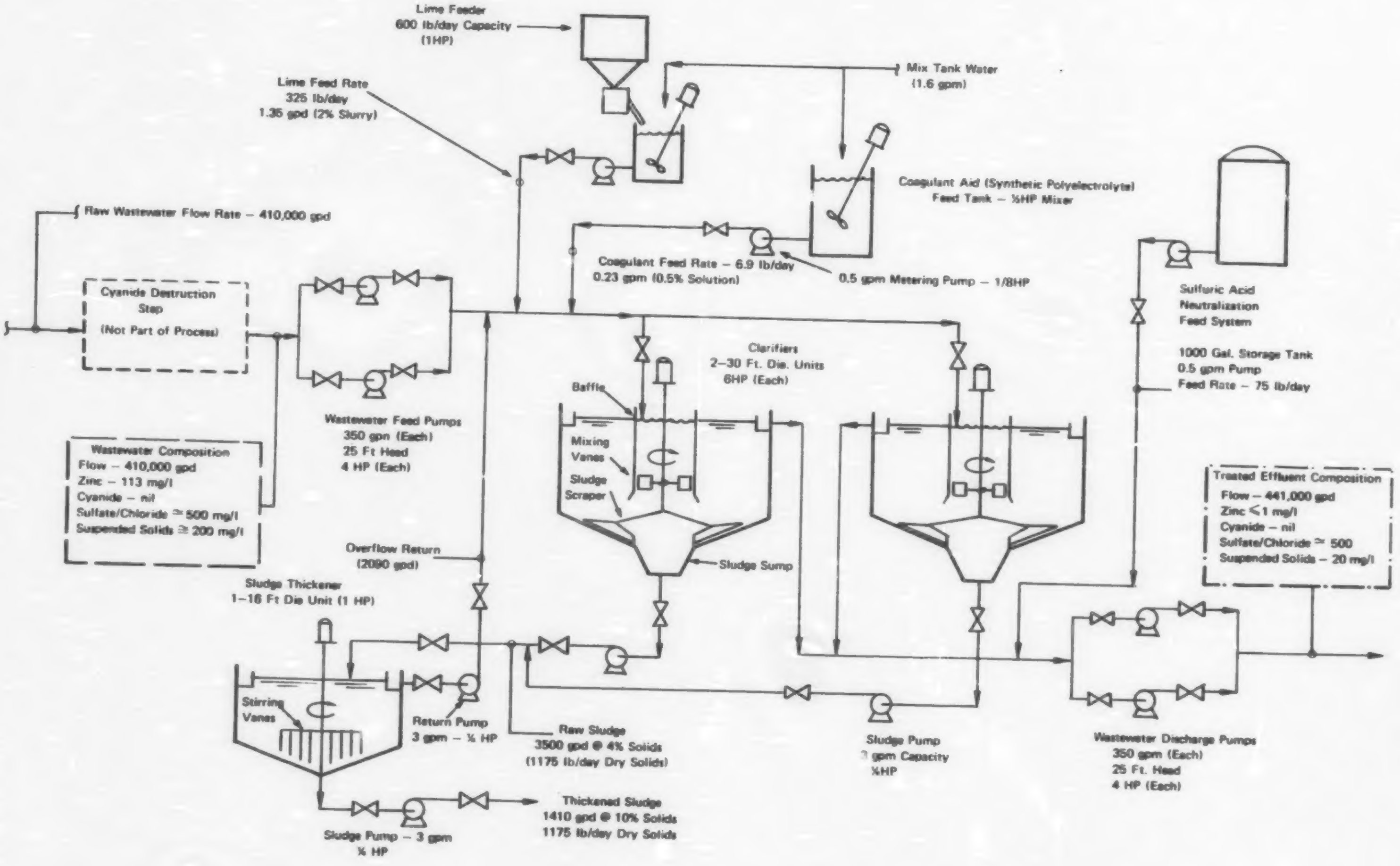

Lime Feeder
600 lb/day Capacity
(1HP)
Mix Tank Water
(1.6 gpm)
Lime Feed Rate
325 lb/day
1.35 gpd (2% Slurry)
Coagulant Aid (Synthetic Polyelectrolyte)
Feed Tank – ½HP Mixer
Raw Wastewater Flow Rate – 410,000 gpd
Coagulant Feed Rate – 6.9 lb/day
0.23 gpm (0.5% Solution)
0.5 gpm Metering Pump – 1/8HP
Sulfuric Acid
Neutralization
Feed System
Cyanide Destruction
Step
(Not Part of Process)
Clarifiers
2–30 Ft. Dia. Units
6HP (Each)
1000 Gal. Storage Tank
0.5 gpm Pump
Feed Rate – 75 lb/day
Baffle
Wastewater Feed Pumps
350 gpn (Each)
25 Ft Head
4 HP (Each)
Mixing
Vanes
Sludge
Scraper
Wastewater Composition
Flow – 410,000 gpd
Zinc – 113 mg/l
Cyanide – nil
Sulfate/Chloride ≃ 500 mg/l
Suspended Solids ≅ 200 mg/l
Treated Effluent Composition
Flow – 441,000 gpd
Zinc ≤ 1 mg/l
Cyanide – nil
Sulfate/Chloride ≃ 500
Suspended Solids – 20 mg/l
Overflow Return
(2090 gpd)
Sludge Sump
Sludge Thickener
1–16 Ft Dia Unit (1 HP)
Stirring
Vanes
Return Pump
3 gpm – ¼ HP
Raw Sludge
3500 gpd @ 4% Solids
(1175 lb/day Dry Solids)
Sludge Pump
3 gpm Capacity
¼HP
Wastewater Discharge Pumps
350 gpm (Each)
25 Ft. Head
4 HP (Each)
Thickened Sludge
1410 gpd @ 10% Solids
1175 lb/day Dry Solids
Sludge Pump – 3 gpm
¼ HP

FIGURE 4 PRECIPITATION, FLOCCULATION, AND SEDIMENTATION – ILLUSTRATIVE FLOW DIAGRAM WASTE STREAM–WASTEWATER FROM AUTOMOTIVE PLATING OPERATION

Referring to Figure 4, a brief description of the process scheme is as follows:

- Wastewater from the cyanide destruction step flows to two parallel clarifiers with an overflow rate of 300 gpd/sq ft. (The design overflow rate is actually 600 gpd/sq ft, thus allowing continued operation when one unit is down for repair or maintenance.)

- Lime is added to the incoming wastewater at a dosage of approximately 50% greater than the stoichiometric amount required to convert all of the soluble zinc to zinc hydroxide precipitates.

- A synthetic polyelectrolyte coagulant aid is also added at a typical dosage of 2 mg/l. (Both the lime and the coagulant aid are fed to the waste stream in the form of an aqueous solution.)

- Since the clarifiers are the type that employ self-contained mixing/flocculating and settling zones, all of the precipitation and flocculation reactions take place in the clarifiers themselves.

- The wet sludge is then pumped to a sludge thickener which allows for further sludge settling and compaction, reducing the sludge volumetric flowrate from 3500 gpd to 1410 gpd, while increasing the sludge solids concentration from 4% to 10%. Depending on site-specific constraints, the sludge from the thickener can either be landfilled directly or subjected to further dewatering steps, such as vacuum filtration or centrifugation.

- The suspended solids in the raw wastewater and the zinc hydroxide precipitate settle to the bottom of the clarifiers and are drawn off as a low solids consistency wet sludge (4% solids by weight).

- Sulfuric acid is fed to the treated effluent in order to return the pH to the neutral range. The treated effluent has a suspended solids concentration of 20 mg/l and a zinc concentration of less than 1.0 mg/l.

Cost estimates were developed for the process scheme depicted in Figure 4, and these are presented in Table 2. The total annual cost is divided into variable costs, which include all the components of the direct operating cost, and fixed costs, which include capital-related items such as capital recovery and taxes and insurance.

For the illustrative system, the total annual cost is $144,000/year, which on a unit cost basis translates to $1.00/1000 gal treated. Such a cost is quite typical for this type of treatment system.

TABLE 2

OPERATING COST ESTIMATES FOR ILLUSTRATIVE PRECIPITATION, FLOCCULATION, AND SEDIMENTATION SYSTEM

Waste Stream: Wastewater from Automotive Plating Operation
Flowrate = 410,000 gpd
Zinc Concentration = 113 mg/l

Capital Investment – $301,000

	Annual Quantity	Cost Per Unit Quantity	Annual Cost ($/yr)
Variable Costs			
Operating Labor (Including supervision plus overhead)	5,600 mh/yr	$12.00/hr	$ 67,200
Maintenance (labor plus materials)	–	–	12,000
Chemicals			
• hydrated lime	57 tons/yr	$35.00/ton	2,000
• coagulant aid	2,420 lb/yr	$ 2.00/lb	4,800
• sulfuric acid	13.1 tons/yr	$60.00/ton	800
Electrical Energy	148,700 kWh/yr	$ 0.02/kWh	3,000
Total Variable Cost			$ 89,800/yr
Fixed Costs			
Capital Recovery (10 years @ 10%)	–	–	48,200
Taxes & Insurance (@ 2% of capital investment)	–	–	6,000
Total Fixed Cost	–	–	$ 54,200
Total Annual Cost	–	–	$ 144,000/yr
Unit Cost (cost per quantity of waste treated)	–	–	$1.00/1000 gal

Notes: 1. (capital investment adjusted to January 1976 (Engineering News Record Construction Cost Index = 2,305)

2. Operating costs are based on a 24-hour per day, 350 day per year operating period.

Source: Arthur D. Little, Inc., estimates

In considering treatment economics in a general sense, it is necessary to take into account economy-of-scale effects. The capital cost of most process equipment does not vary linearly with size, but rather, as the 0.5-0.8 power of size. Thus, tripling the size of a piece of equipment will not triple the capital cost but will merely double that cost. To illustrate this effect, two additional cost estimates were prepared – one for a treatment system one-fifth the size of that used in the example, and one for a system five times its size.

As can be seen from Table 3, over a 25-fold size range, the unit treatment cost for the illustrative treatment system varies from $2.43/1000 gal for the small system to $0.48/1000 gal for the large system.

TABLE 3

PRECIPITATION, FLOCCULATION, AND SEDIMENTATION COST ESTIMATES AS A FUNCTION OF SIZE

	Treatment System Size (Wastewater Flowrate		
	82,000 gpd	**410,000 gpd**	**2,050,000 gpd**
Capital Investment	$106,000	$301,000	$857,000
Variable Cost			
Labor	44,400	67,200	101,000
Maintenance	4,200	12,000	34,300
Chemicals			
• Lime	400	2,000	10,000
• Coagulant Acid	970	4,800	24,200
• Sulfuric Acid	160	3,000	3,900
Electrical Energy	600	3,000	14,900
Total Variable Cost	$ 50,700/yr	$ 89,800/yr	$188,300/yr
Fixed Cost			
Capital Recovery	17,000	48,200	137,100
Taxes and Insurance	2,100	6,000	17,100
Total Fixed Cost	$ 19,100/yr	$ 54,200/yr	$154,200
Total Annual Cost	$ 69,800/yr	$144,000/yr	$342,500
Unit Cost ($/1000 Gal)	$2.43/1000 gal	$1.00/1000 gal.	$0.48/1000 gal

Notes: All costs are for the waste stream and treatment process scheme depicted in Figure 4 of this study.

Source: Arthur D. Little, Inc., estimates

To provide perspective on the types of costs that can be expected, the following strictly general costs ranges are presented:

- A large (over 5 million gpd) system employing only sedimentation, with no flocculating chemicals used, will typically treat wastewater at a cost of \$0.10-\$0.50/1000 gal treated (amortization plus operating costs).
- A moderate size (0.5-5 million gpd) system employing precipitation, flocculation, and sedimentation and using moderate dosages of normally used precipitating/flocculating agents will usually treat wastewater at a cost of \$0.50-\$3.00/1000 gal.
- Small, specially designed systems (less than 0.5 million gpd), using high dosages of precipitating/flocculating agents can have costs that are much higher, but these will rarely exceed \$6.00 per 1000 gal, because the cost level treatment methods would be given preference because of efficiencies, and so on.

Compared to other processes, such as carbon adsorption or distillation, used in the treatment of hazardous wastes, precipitation, flocculation, and sedimentation are generally considered rather low cost processes.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

A. PRECIPITATION

Theoretically, when applying precipitation to the removal of toxic or hazardous materials (such as heavy metals) from aqueous waste streams, it should be possible to achieve an effluent concentration of the particular ion of concern equal to the solubility of the ion in relation to its precipitated solid phase. In theory, the solubilities of the hydroxides of iron, zinc, chromium, mercury, lead, copper, and many other heavy metals are less than 1.0 ppm, under slightly alkaline conditions. Actual attempts at precipitating these metals from real aqueous waste streams generally do not achieve effluent concentrations equal to the theoretical solubility limits for a variety of reasons, some of which are listed below:

1. Many metals exhibit a strong tendency to form organo-metallic complexes with a variety of natural and synthetic organic compounds. Often, these complexes are far more soluble than the ion by itself, and the presence of complexes can often impede many precipitation reactions. Cyanide ion can form complexes with a number of metallic ions, resulting in a situation in which it is difficult both to destroy the cyanide by oxidation and to precipitate the metal as a hydroxide or sulfide. Many amine compounds also form metal complexes.

2. Even though adequate flocculation and sedimentation may be applied, it is never possible to cause all of the precipitated particles to form readily settleable floc particles. Thus while the desired ions may be removed from solutions and transformed into suspended solid particles, a certain fraction of those particles is generally too small in size to be removed by conventional means.

3. Metal ions can sometimes adsorb onto the surfaces of colloidal organic or inorganic solid particles. In such cases it is often difficult to completely isolate the desired metal ion from other components of the waste stream.

In spite of such impeding influences, it is often possible to achieve metal ion concentrations in the treated effluent which are within an order of magnitude of the theoretical solubility limit. Frequently when a slightly acidic waste is treated with lime (which always contains some $CaCO_3$), CO_2 is liberated in the waste and most effectively reduces the solubilities of the various metal species by producing basic carbonates, i.e., metal hydroxide and metal carbonate.

Where several metal ions are present in a given waste stream and where there is a very high concentration of colloidal yet potentially settleable (through flocculation) inert solids, it is seldom possible to effect a sharp separation of the various metal species by means of precipitation. Due to coprecipitation effects, in which two or more ions precipitate together as a single compound, and due to the tendency for many inert colloidal particles to flocculate and settle with the desired precipitated metal, it is often not possible to isolate a particular hazardous metallic species as a pure hydroxide or sulfide sludge. Often, the metal is lost within the total sludge matrix consisting of other metal precipitates and/or settled particles.

B. FLOCCULATION

While it is generally possible, through the selection and use of the proper flocculating agents, to achieve at least some degree of flocculation in most waste streams containing suspended solids, flocculation is seldom complete, and there is always a certain fraction of particles which do not properly flocculate. In many cases, excessively high dosages of flocculating agents must be used, thus contributing to the total sludge volume as a result of their mass.

C. SEDIMENTATION

Due to the inevitable particle size distribution found in even well-flocculated waste streams, a certain fraction of particles will not be removed by even the best designed sedimentation device. In spite of this limitation, most clarifiers used in water and wastewater treatment applications are capable of producing treated effluents with typically suspended solids concentration in the range of 10-200 ppm. Since the raw waste stream may often contain a suspended solids concentration of over 10,000 ppm, clarifiers can generally effect 90-99% removal of suspended solids.

Sludge thickening applications are generally less effective in terms of percent removal. A sludge thickener will typically accept a sludge that is 2-15% solids and produce a more concentrated sludge that is 4-30% solids. Although a sludge thickener is generally capable of producing only a 2-5-fold concentration effect, it is very useful in that it allows for a reduced size, and hence cost, of subsequent dewatering steps, such as vacuum filtration or centrifugation.

D. ADVANTAGES AND DISADVANTAGES

Listed below are the major advantages and disadvantages of the processes as applied to hazardous wastes.

Advantages

- *Operational Practicality* – The processes have been in use for many years, the equipment is relatively simple and readily commercially available, and the processes are relatively easy to operate.
- *Versatility* – The processes can be applied to almost any liquid waste stream containing precipitable and/or settleable hazardous wastes.

- *Relatively Low Cost* – Due to their relatively low cost, the processes can economically be applied to very large volumes of waste liquids.

- *Low Energy Consumption* – Energy consumption is a small fraction of the total treatment cost. Therefore, these processes will not be overly penalized by rising energy prices.

- *Easily Integrated into More Complex Treatment Systems* – Precipitation, flocculation, and sedimentation are often used as a preliminary treatment step in conjunction with more advanced treatment processes.

- *Potential for Waste Recovery* – Precipitation, flocculation, and sedimentation are non-destructive processes. This feature is an advantage if waste recovery is deemed feasible.

Disadvantages

- *Possibility of Incomplete Removal* – Although the solubility of many metallic compounds is extremely low, complexation with organic substances can seriously interfere with the removal process. Also, many precipitates (notably sulfides) tend to form very small, difficult-to-flocculate particles which are poorly removed in the sedimentation step.

- *Non-Selectivity* – Very often, non-hazardous materials are removed along with the target hazardous materials, thus diluting and enlarging the solid waste stream that must be disposed of. For example, in the lime precipitation of heavy metals from wastewater, large quantities of naturally occurring non-hazardous calcium are precipitated along with the metals.

- *Production of a Wet Ultimate Product.*– As discussed, the solids that are removed are accompanied by a portion of the original liquid. While in many cases this is not a serious problem, it is by no means an attractive feature.

- *Non-Destructive* – What was listed as an advantage in cases where waste recovery is feasible is actually a disadvantage in cases where the waste is of no recoverable value and is exceedingly hazardous. While precipitated metal compounds are generally less hazardous than metal ions in solution, metal precipitates are by no means innocuous from an environmental point of view.

For the most part, the processes of precipitation, flocculation, and sedimentation are "mature" processes from an engineering/technical standpoint. Most developmental work is focused on two areas:

1. Efforts by equipment suppliers to improve equipment performance and reduce equipment costs.

2. Efforts by both equipment suppliers and people with waste treatment problems to test these processes on specific wastes.

While some theoretical research is being performed on the university level, only a small percentage of this is directly applicable to the design and selection of actual waste treatment systems. Based on our knowledge of the state of the art and our contact with knowledgeable parties in the pollution control field, we do not believe that there are any major technical innovations involving the use of precipitation, flocculation, and sedimentation that are about to be implemented that will radically alter or greatly expand the use of these processes.

With regard to specific hazardous waste applications, we perceive the following problem to exist in many instances – people with hazardous waste streams that are small in volume (less than 10,000 gpd) will have difficulty in obtaining readily available commercial equipment. Most suppliers of equipment for precipitation, flocculation, and sedimentation are geared toward marketing their systems to customers with large wastewater streams. It is simply uneconomical for major equipment suppliers to focus on small treatment systems. As a result, some of the small systems tend to be "homemade" or specially constructed by either the user or his consultant engineer. In addition, there are very few batch precipitation, flocculation, and sedimentation systems in operation.

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21. Scott, D.S., and Horlings, H., "Removal of Phosphates and Metals from Sewage Sludges," *Environ. Sci. & Tech.*, 9: 846-855, 1975.

22. Private communication – (based on ADL visits).

23. Personal communication– Gulf States Paper Co., Tuscaloosa, Alabama.

B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD

1. The Ecodyne Corp., Industrial Waste Treatment Division
   U.S. Highway, Route 22
   Union, N.J.

2. The Permutit Co.
   Princeton, N.J.

3. Dr. John Ciancia
   U.S. Environmental Protection Agency
   National Environmental Research Center
   Edison, N.J.

4. The Silresim Chemical Co.
   Lowell, Ma.

5. Chem-Trol Pollution Services, Inc.
   Model City, N.Y.

FLOTATION

Prepared by:

William I. Watson

I. CONCLUSIONS AND RECOMMENDATIONS

Flotation processes are widely used, particularly in ore processing. Many other uses, while suggested, have not found commercial application. As to waste stream treatment, the only related use is for the recycling of cellulose from waste paper where a flotation process is used in the removal of ink. The flotation process is potentially useful for separating different types of solid particles suspended in a liquid medium. However, even though the technology is well understood and expertise is readily available for any application which might be considered, flotation is not likely to see widespread usage in industrial waste treatment. This is because the processing costs are on the order of dollars per ton of solid materials processed.

II. PROCESS DESCRIPTION

A. BACKGROUND AND UNDERLYING PRINCIPLES

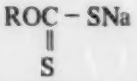
Flotation is a process of ore concentration developed and used principally by the mineral industry. Valuable ore constituents are separated as a "concentrate" from the waste products called "tailings."

The process is a physical-chemical method (carried out in a wet environment) for concentrating finely ground ores. A necessary and important step to prepare the ore for flotation is crushing and grinding, which is designed for each particular application to separate the individual mineral particles that make up the ore by reducing them to their natural grain size. Also, in some cases, the removal of "slimes" is necessary before flotation.

The flotation process itself involves chemical treatment of an ore pulp or slurry to create conditions favorable for the attachment of selected mineral particles to air bubbles formed therein. The air bubbles carry the selected minerals to the surface of the pulp and form a stabilized froth which is skimmed off while the other waste minerals remain in the pulp.

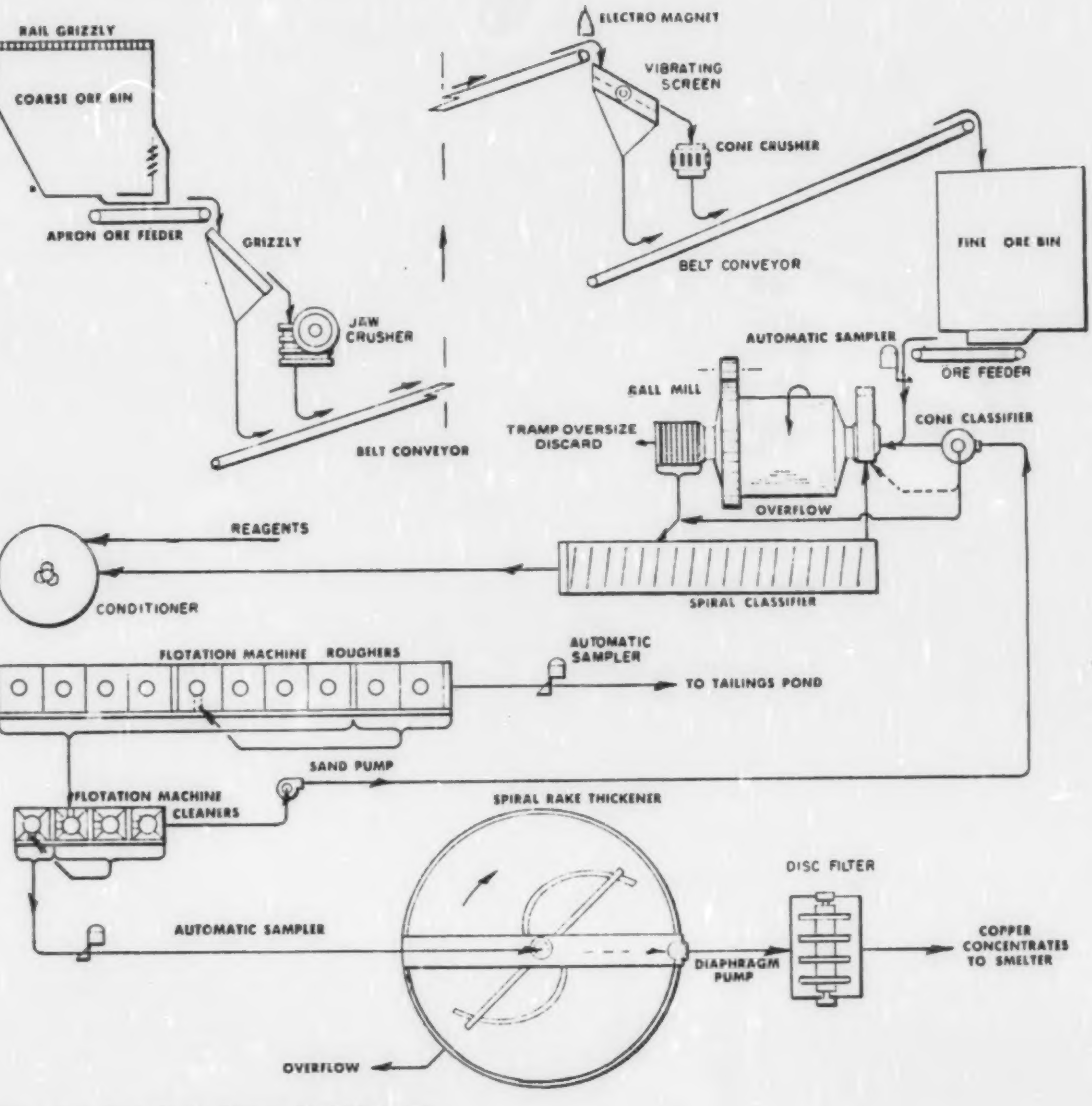
The process of contacting the ground ore pulp with reagents is called "conditioning" and is usually done with reagents being added in an agitator for mixing with the pulp just before flotation However, at times, benefits are obtained by adding reagents in the grinding stage. A sketch of a typical flotation flowsheet is shown in Figure 1.

The ability of an air bubble to pick up a heavy mineral sulfide particle is illustrated in Figure 2. The mechanism of collection and attachment is generally well understood. For example, in the text accompanying the drawing in Figure 2, xanthate as a collector for galena is described. Xanthate, the collector molecule, has a hydrocarbon chain with a sulfur attached as follows:



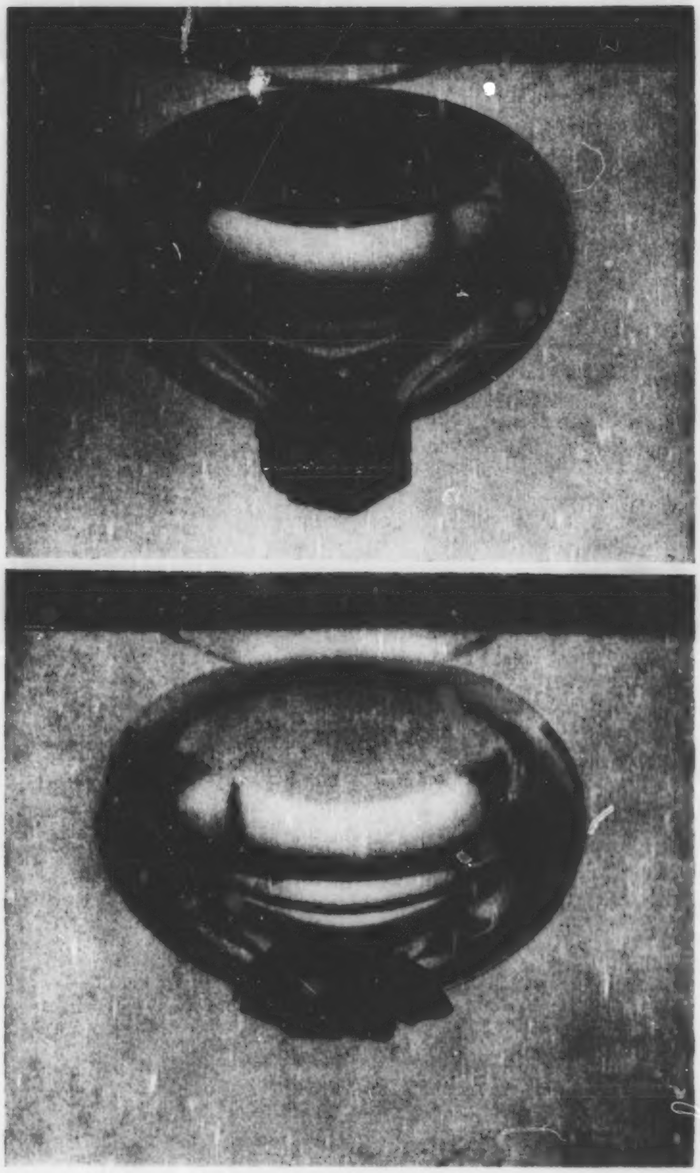
$$\mathrm{RO}\underset{\underset{\displaystyle\mathrm{S}}{\|}}{\mathrm{C}}-\mathrm{SNa} \qquad \mathrm{R} = \text{hydrocarbon group}$$

In collection, the sodium ion goes into solution, leaving the free sulfur atom to attach to and fit into the Pb-S atomic structure of the galena surface, leaving the hydrocarbon chain sticking out. This makes the galena surface hydrophobic and pushes the galena grains into the air bubble which lifts them to the surface. The collection and flotation of other minerals with various types of reagents in general functions in the same way.


RAIL GRIZZLY
COARSE ORE BIN
APRON ORE FEEDER
GRIZZLY
JAW CRUSHER
BELT CONVEYOR
ELECTRO MAGNET
VIBRATING SCREEN
CONE CRUSHER
BELT CONVEYOR
FINE ORE BIN
AUTOMATIC SAMPLER
ORE FEEDER
BALL MILL
CONE CLASSIFIER
TRAMP OVERSIZE DISCARD
OVERFLOW
REAGENTS
SPIRAL CLASSIFIER
CONDITIONER
FLOTATION MACHINE ROUGHERS
AUTOMATIC SAMPLER
TO TAILINGS POND
SAND PUMP
FLOTATION MACHINE CLEANERS
SPIRAL RAKE THICKENER
DISC FILTER
AUTOMATIC SAMPLER
DIAPHRAGM PUMP
COPPER CONCENTRATES TO SMELTER
OVERFLOW

Source: Flowsheet Study Denver Equipment Co.

FIGURE 1 TYPICAL ORE FLOTATION FLOWSHEET



Source: *Principles of Flotation,* Southerland and Wark, Australasian Institute of Mining and Metallurgy, 1955.

FIGURE 2 **THE ADHESION OF MINERAL PARTICLES TO AN AIR BUBBLE (Galena Particles – PbS)**

The selectivity of the process can be very good. For example, it is possible to separate KCl from NaCl, two very similar salt type minerals, by using the right reagent and conditions.

B. OPERATING CHARACTERISTICS

The flotation process as previously stated is particularly useful for removing selected portions from mixtures of solid materials such as ores. Ores are aggregates of minerals in which any number of distinct minerals can be present. By grinding to the appropriate size, the contained minerals can be physically separated from each other and then be selectively removed from the physical mixture by any number of processes such as sedimentation, tabling, and flotation. In flotation, ground ore or mineral mixtures are mixed with water to form a slurry or pulp for flotation treatment. In principle, however, the flotation method can be used with liquid media other than water and can be used for emulsions, sludges, slurries or any physical mixtures which can be converted into such suspensions in a liquid medium. Flotation is not restricted to any particular group of materials, but as stated is most prevalently used for ore and mineral separation with the useful products to be separated out generally present in amounts less than ten percent.

1. Reagents

The operation of the flotation process is based on the use of chemical reagents that selectively will attach to and alter the surface characteristics of the mineral particles to be floated. Such reagents are called "collectors." A whole spectrum of reagents has to be considered to meet the various requirements of the flotation process. Common flotation reagents are grouped as follows:

- *Modifiers* – Basically used to control the pH of the separation which is crucial in many cases. They are acids, lime, soda ash, and caustic soda.

- *Activators* – Used to "activate" or prepare the mineral surface for the collector. They are chemicals such as sodium sulfide and copper sulfate.

- *Depressants* – Used to prevent flotation of minerals that one does not want to float. They are chemicals such as dextrin, sodium cyanide, starch, and guar gum.

- *Collectors* – This group of reagents can be divided into three specific groups as follows:

    - Anionic – for floating non-sulfide minerals: xanthates, dithiophosphates, thiocarbanilide, thionocarbamates, xanthogen formates, etc.

  - Anionic – for floating non-sulfide minerals: fatty acids of various types.
  - Cationic – for floating non-sulfide minerals: alkyl amines and quaternary ammonium salts.

- *Frothers* – Used to form a reasonably stable froth so the collected particles can be recovered. They are chemicals such as pine oil and cresylic acid, but today M.I.B.C. (methyl isobutyl carbinol) is almost the universally used frother.

- *Flocculants* – Used in the thickening operation following flotation. Lime or some of the high molecular weight, water soluble, non-ionic polyacrylamides are most commonly used.

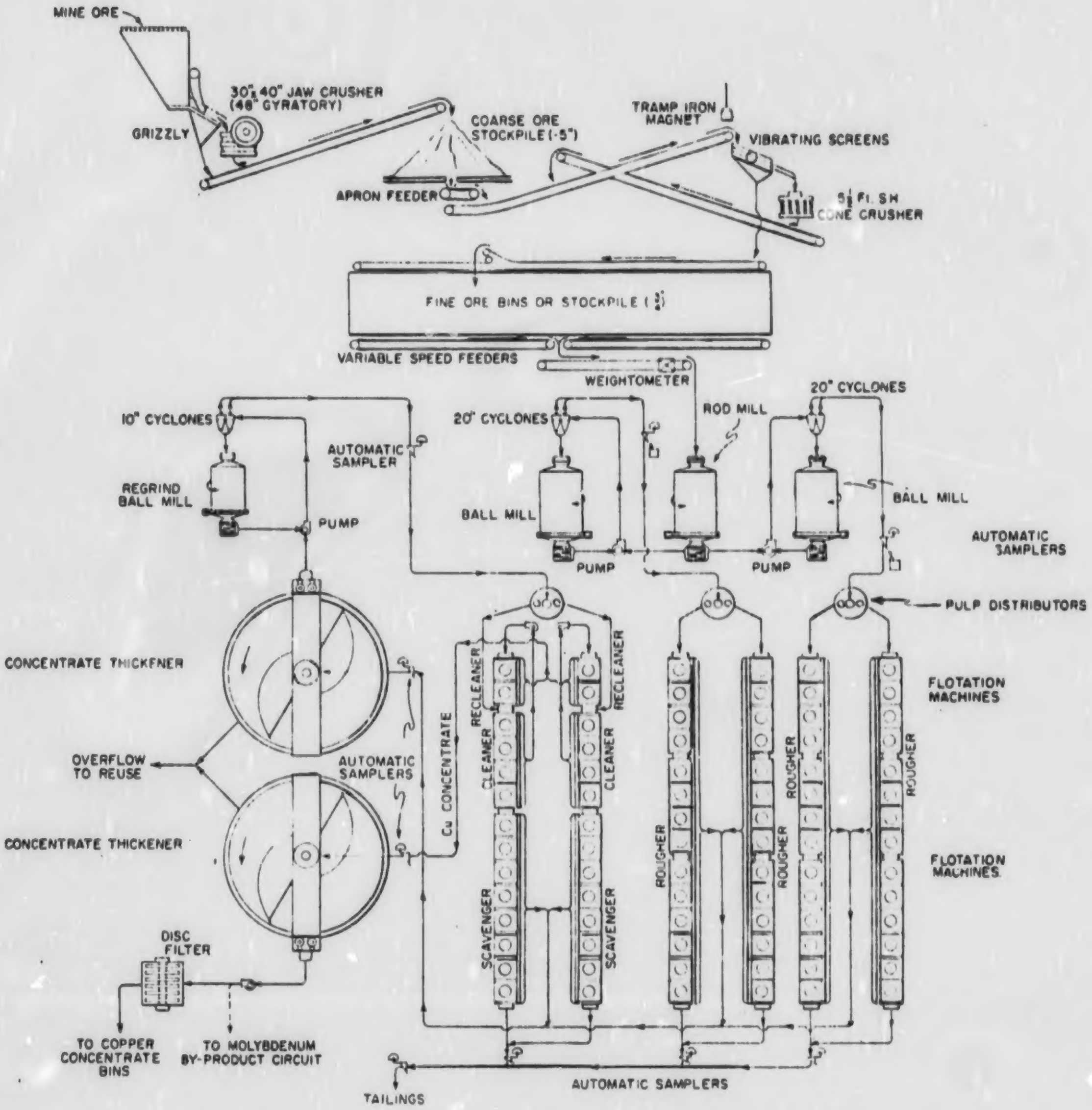
2. Process Operation

The actual flotation separation is carried out in "flotation cells" which are only a small part of the overall process as indicated in Figure 1 and in Figure 3, which is a typical flowsheet for a large porphyry copper operation where copper sulfide minerals are separated from the waste rock.

The flotation cell is a simple tank with an agitator mechanism with means to admit air at the bottom. Cells can be from 10 to 200 cu ft in size depending on the separation being made and the tonnage being processed. Large plants can have many hundreds of cells. The agitation, with the introduced air, forms tiny air bubbles which contact the prepared particles and bring them to the surface where they overflow the top of the cell or are at times removed or assisted with paddle wheel scrapers.

Many flotations are carried out where only one valuable component is separated from a waste material. However, many others separate two, three or even four valuable products from the waste material. In this case, the process is usually referred to as "differential flotation." A good example of this is the case of mixed sulfides ores of copper, lead, and zinc. In this operation, separate copper, lead, iron, and zinc concentrates can be produced by suitable selection of flotation conditions and reagents. Another example in the nonmetallic area is the flotation of pegmatites where separate concentrates of mica, spodumene, feldspar, and quartz can be produced.

Flotation can also be done in a liquid medium other than plain water. For example, soluble salts are floated in saturated brine solutions, and some flotations are carried out using sea water where fresh water is scarce.


MINE ORE
GRIZZLY
30" x 40" JAW CRUSHER (48" GYRATORY)
COARSE ORE STOCKPILE (-5")
APRON FEEDER
TRAMP IRON MAGNET
VIBRATING SCREENS
5½ Ft. SH CONE CRUSHER
FINE ORE BINS OR STOCKPILE (¾")
VARIABLE SPEED FEEDERS
WEIGHTOMETER
10" CYCLONES
20" CYCLONES
ROD MILL
20" CYCLONES
AUTOMATIC SAMPLER
REGRIND BALL MILL
BALL MILL
BALL MILL
PUMP
PUMP
PUMP
AUTOMATIC SAMPLERS
PULP DISTRIBUTORS
CONCENTRATE THICKENER
RECLEANER
RECLEANER
CLEANER
CLEANER
Cu CONCENTRATE
FLOTATION MACHINES
ROUGHER
ROUGHER
ROUGHER
ROUGHER
OVERFLOW TO REUSE
AUTOMATIC SAMPLERS
CONCENTRATE THICKENER
FLOTATION MACHINES
SCAVENGER
SCAVENGER
DISC FILTER
TO COPPER CONCENTRATE BINS
TO MOLYBDENUM BY-PRODUCT CIRCUIT
TAILINGS
AUTOMATIC SAMPLERS

Source: Flowsheet Study Denver Equipment Co.

FIGURE 3 FLOTATION PROCESS FLOWSHEET – TYPICAL SULFIDE COPPER ORE

3. Variations of the Process and Adaptations

While the flotation process has been applied principally to mineral processing, there have been a number of applications and potential applications in related as well as different areas. Some of the more important of these are briefly described below.

a. Flotation of Microorganisms

Research work has shown that bacteria can be floated and concentrated from the aqueous phase (Ref. 1). It was found that for the organisms used in this study, sodium chloride acted as a collector and the organisms could be floated.

b. Flotation of Waste Paper

Flotation is used to treat paper pulp mixtures of magazines, newspapers, and other paper rejects to remove ink, pigments, and coatings. The clean cellulose fiber can then be reused to make specialty grade papers. In 1974 there were three plants in the United States which treated about 25,000 tons of paper a year.

c. Precipitate Flotation

It is possible to float precipitates that have been made in a solution and recover them as a froth concentrate. In this application the metal to be removed from solution is precipitated before the addition of a collector.

One example of this in the mineral processing industry is the leach-precipitation-flotation process (L.P.F.) which is used on mixed oxide-sulfide copper ores. In the L.P.F. process, the ore is treated with sulfuric acid which dissolves the oxide copper minerals. Powdered iron is then added to the slurry which precipitates the copper as metallic copper particles. The whole mixture is then floated, and the precipitated copper as well as the unaffected sulfide copper particles are collected as a froth concentrate.

Another possible application of precipitate flotation is the flotation of complexed cyanide as a means of removing cyanide from solutions or mixed suspensions. If ferrous iron is added to a cyanide-containing solution, a ferro-cyanide precipitate can be formed which can then be floated from the solution. Test results in one case (Ref. 6) indicated that about 95% of the complexed cyanide could be removed under the proper conditions.

d. Agglomerate Flotation (Emulsion Flotation)

The typical flotation process takes place on ground ores where the top particle size is on the order of 40 mesh (about 400 microns). It is difficult for an air bubble to pick up a particle much bigger than that.

However, coarser particles up to about 10 mesh in size (2000 microns) can be floated after conditioning by carrying out the separation on a vibrating table or similar device. This is called agglomerate or table flotation, and is practiced in the phosphate industry where coarse apatite particles are separated from quartz grains using a fatty acid-fuel oil emulsion as a collector.

e. Ion Exchanger Flotation

Work has shown that ion-exchange resins can be contacted with solutions to pick up or exchange particular ions in the solution. The resin particles can then be removed by flotation. There is no application of this process as far as we know. Resin particles can usually be more simply removed by screening.

f. Ion Flotation

In ion flotation a surfactant ion of opposite charge to the inorganic ion to be removed from solution is added in stoichiometric amounts. The surfactant "collector" must be added in such a way that it exists in solution as simple ions. The collector reacts with the inorganic ion to form an insoluble "soap" which can be levitated to the surface with a gentle bubbling action to form a foam or scum which can be removed.

One ion flotation system that has been investigated was the removal of dissolved copper with a sodium lauryl sulfate collector (Ref. 8). There are no practical operating plants using the technique as far as we know.

Other systems that have been studied have involved the ion flotation of cadmium, nickel, and iron cyanide complexes with collectors such as dodecylamine chloride.

The possibilities for these kinds of separations are almost unlimited if specific and selective "soaps" can be developed.

g. Foam Fractionation

This is a process for concentrating metals in solution and is not strictly a flotation process. However, some confusion exists, so it is briefly described here.

When a solution containing surface active solutes is exposed to a gas, the solutes tend to migrate to the gas-liquid interface. Therefore, the surface layer is richer in the solute than the bulk of the liquid. Therefore, when gas is bubbled through such a solution, it foams and creates a large amount of surface. Collecting the froth on the surface will yield a concentrate rich in the desired solute.

Such foaming systems have only two phases, a gas and a liquid, and thus differ from the usual flotation processes with their solid phases as well as a gaseous and liquid phase.

III. APPLICATIONS TO DATE

A. PRINCIPAL CURRENT APPLICATIONS

The flotation process is widely used in the mineral industry and in fact is probably the most important mineral concentrating process developed in the last one hundred years. It is certainly the single most important process that has made it possible to economically treat lower and lower grade metallic and non-metallic ores.

In 1970, 405,254,000 short tons of ore were treated by the flotation process producing 54,144,000 tons of concentrate (see Table 1). There were 240 flotation plants in operation in 33 states processing 27 different types of ores.

Table 1 lists the consumption of reagents in flotation plants for 1970. It can be seen that overall about two billion lbs were used (or about 5 lbs/ton of ore processed).

B. POTENTIAL APPLICATIONS TO WASTE TREATMENT

It is our belief that if enough research and development were carried out on the system, almost any two or three solid component mixtures (in the proper size range) could be processed by flotation techniques resulting in separation of the components.

The hazardous waste forms that can possibly be handled by conventional flotation are slurries, sludges, or any solid mixture in an aqueous or possibly non-aqueous solution. The best application for the process as indicated above is for separating, say, a hazardous solid from one that is not. Thus, any single solid component type in a slurry could be floated. This component would be recovered as a froth concentrate which would require further processing by thickening and/or filtration for recovery as a moist solid filter cake. This could then be dried or processed in any way necessary for reuse, sale, storage or safe disposal.

The ion and precipitate flotation variations of the flotation process discussed previously could be used for the removal of some hazardous materials in solution. Specific examples of ions which might be removed by flotation are: heavy metal ions (copper, nickel, cadmium) and cyanides. We believe many other heavy metal ions might also be amenable to removal by these processes, as well as other inorganics such as carbonyls and fluorides. However, as far as we know, no work has been done on ion or precipitate flotation of materials other than those mentioned above.

There is another aspect of the flotation process that must be considered. Many different reagents can be and are used. Though the process is operated with just enough

TABLE 1 CONSUMPTION OF REAGENTS BY TYPES AND PLANTS IN FROTH FLOTATION IN 1970

Type of plant	Reagent consumption (pounds)													
	Modifiers		Activators		Depressants		Collectors		Frothers		Flocculants		Total	
	Total	Per ton	Total	Per ton	Total	Per ton	Total	Per ton	Total	Per ton	Total	Per ton	Total	Per ton
Copper	640,370,297	8.063	158,388	0.078	63,229	0.006	6,953,885	0.087	3,799,912	0.048	337,308	0.006	651,683,019	8.169
Copper-molybdenum	497,176,970	3.188	---------	-----	6,135,382	.054	9,911,134	.064	12,718,876	.082	2,154,075	.028	[1]528,123,127	[1]3.387
Copper-lead-zinc	5,437,763	1.000	941,291	.110	5,827,811	.626	1,089,490	.116	375,550	.040	28,062	.012	13,699,967	1.464
Copper-zinc-iron	26,605,063	9.098	1,268,438	.716	332,523	.191	990,692	.310	306,432	.096	13,813	.005	29,516,961	9.244
Gold-silver	187,310	2.495	---------	-----	---------	-----	25,524	.263	742	.040	2,102	.028	215,678	2.224
Lead-zinc	2,964,458	.885	1,664,698	.414	1,079,914	.269	604,799	.151	354,029	.088	14,077	.077	[1]6,772,600	[1]1.685
Lead-zinc-silver	5,314,197	2.081	2,584,263	.938	1,553,862	.564	760,455	.274	495,397	.178	21,219	.014	[1]10,748,178	[1]3.870
Zinc	798,165	3.369	1,854,761	.494	28,248	.070	250,072	.067	220,766	.059	---------	-----	3,152,012	.840
Barite	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Bastnaesite	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Feldspar-mica-quartz	8,093,208	3.953	---------	-----	301,500	.900	3,547,776	1.664	353,823	.264	26,761	.059	12,323,068	5.779
Fluorspar	6,207,827	14.835	365,588	.946	1,041,121	2.695	419,652	1.003	124,376	.322	963	.030	8,159,527	19.498
Garnet	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Ilmenite	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Iron ores	23,630,257	4.379	---------	-----	210,518	.343	26,672,577	.978	51,811	.024	205,029	.015	50,770,192	1.861
Kyanite	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Limestone-magnesite	888,853	4.441	---------	-----	993,730	4.965	3,171,029	2.898	59,342	.219	15,242	.015	5,128,196	4.686
Mercury	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Molybdenum	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Phosphate	134,346,171	2.150	---------	-----	---------	-----	515,594,226	7.958	688,683	.069	28,000	.056	650,657,080	10.042
Potash	10,888,518	1.200	---------	-----	6,220,460	.641	5,021,954	.429	1,670,253	.143	646,314	.063	24,447,499	2.089
Talc	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Tungsten	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Vermiculite	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Anthracite	---------	-----	---------	-----	---------	-----	3,505,729	2.836	395,019	.320	---------	-----	3,900,748	3.156
Bituminous coal	2,716,208	2.861	---------	-----	---------	-----	4,265,992	1.657	2,168,955	.192	2,204,030	.209	11,355,185	.965
Total	1,396,337,689	3.938	8,971,913	.382	28,937,078	.164	600,392,057	1.521	26,204,468	.082	5,798,638	.032	[1]2,066,777,943	[1]5.114

W Withheld to avoid disclosing individual company confidential data; included in "Total."

[1] Includes other reagents as follows: Copper-molybdenum, 26,690 pounds (0.003 pound per ton); lead-zinc, 90,625 pounds (0.060 pound per ton); lead-zinc-silver, 18,785 pounds (0.080 pound per ton); and total, 136,100 pounds (0.014 pound per ton).

Source: U.S.B.M. – Minerals Yearbook 1970.

reagent to make the required separation, some reagents can still appear in the waste tailings discarded from the process.

Most of the added reagents are more or less consumed during the flotation process due to adsorption on the mineral surfaces or complexing with the appropriate ions in solution. Trace amounts of organic reagents, such as hydrocarbons, alcohols, and esters are left in the tailings water, evaporate, decompose, or biodegrade. However, some toxic reagents, if used in flotation carelessly, can constitute a hazard, and great care must be exercised in their use and control. Table 2 is a listing (Ref. 9) of many of the common reagents used in conventional mineral flotation, the typical amount added, the distribution, and potentially toxic species.

TABLE 2

ENVIRONMENTAL CONSIDERATIONS FOR COMMON FLOTATION REAGENTS

Reagent Type & Name	Chemical Composition	Amount Added (lbs/ton)	Reagents Distribution		Toxic Species
			Solids	Solution	
Collectors					
Xanthate	ROCSSH	< 0.1	Mostly complexed	Minor	CS_2
Thiophosphates	$(RO)_2PSSH$	< 0.1	Mostly complexed	Minor	$H_2PO_4^-$, HS^-, H_2S
Fatty acids	RCOOH	0.5 to 2.0	Complexed with minerals and ions	Minor	Biodegradable
Sulfonates and Sulfates	RSO_3H RSO_4	0.5 to 2.0	Complexed with minerals and ions	Minor	Biodegradable (except Cyclic)
Amines	RNH_2Ac	0.2 to 2.0	Adsorbed on silicates	Minor	Free amine*
Fuel oils	Saturated	0.1	Selectively adsorbed	Minor	Volatile hydrocarbons
Frothers					
Pine oil	Aromatic alcohols	< 0.1	Carried over in froth	Appreciable	Volatile, carcinogenic
Dow froth	Higher alcohols	< 0.1	Carried over in froth	Appreciable	Volatile, biodegradable
MIBC	Methyl isobutyl-carbinol	< 0.1	Carried over in froth	Appreciable	Volatile, biodegradable
Conditioners					
Sodium sulfides	Na_2S, NaHS	1 to 15	Selectively complexed	Major	HS^-, H_2S, $SO_4^=$
Phosphorus Pentasulfide	P_2S_5	1 to 4	Selectively complexed	Major	HS^-, H_2S
Sodium Cyanide	NaCN	0.005 to 0.1	Mostly complexed	Minor	CN^-
Sodium Silicate	Na_2SiO_3	0.2 to 1.0	Mostly complexed	Appreciable	H_4,SiO_4
Milk of Lime	$Ca(OH)_2$	1 to 4	Mostly complexed	Appreciable	OH^-
Separan	Polyacrylamid	< 0.01	Mostly adsorbed	Minor	Biodegradable

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*Unknown toxicity

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

The typical overall conventional flotation plant is a reasonably large consumer of electrical energy. Most of this energy is used in the size reduction or grinding stage of the process. A typical consumption is shown below:

	kWh/Ton Milled
Crushing	1.58
Grinding	8.29
Flotation and Conditioning	2.48
Pumping	0.88
Thickening and Filtration	0.44
Miscellaneous	1.46
	15.13*

*Can actually vary from 10-40 depending principally on the ore hardness.
Figures shown are averages for 20 large flotation plants.

As can be seen, only about 15% of the total energy consumed is in the actual flotation step itself.

B. ENVIRONMENTAL IMPACTS

As indicated before, flotation is a step which by itself makes a concentrate and a tailing, both of which are further handled and processed.

Air emissions are not of any significance in flotation since it is a wet process. However, in the preparation of an ore or waste for flotation, if the initial crushing step is dry, dust emissions will likely occur at the crusher and at conveyor transfer points. Modern ore crushing plants control these emissions with dust collecting hoods on the crushers and other dust sources. Also, water sprays are used as required on outdoor stockpiles and other dust generating areas.

The waste effluent stream of importance is the flotation tailings which is the waste material after separation of the valuable minerals. In some ore processing plants, this flows directly to a tailings dam and in others it is thickened (to reclaim the water) and then discarded to the tailings dam.

All of these plants have substantial tailings dams from which most recycle water after the solids settle to the bottom. A few of the plants in wet climates discharge water from the tailings dam to public waters, but most of the large copper flotation plants in the Southwest reuse all their water and have zero discharge. For waste treatment, similar problems may be encountered, especially if large volumes of waste are processed.

C ECONOMIC ANALYSIS

In the conventional ore flotation process, the costs are quite variable depending on the size and the nature of the flotation process being practiced. However, it is possible to give some rough estimates for the direct operating cost of various unit operations for different sized plants carrying out typical sulfide ore flotations. These are shown in Table 3.

TABLE 3

COSTS OF VARIOUS UNIT OPERATIONS

	$/Ton Ore Processed		
	500 T/Day	2,000 T/Day	10,000 T/Day
Crushing	0.56	0.29	0.18
Grinding and Classification	1.05	0.81	0.68
Flotation* and Conditioning	1.00	0.82	0.27
Plant Pumping	0.33	0.27	0.09
Thickening and Filtering	0.25	0.10	0.03
Miscellaneous – Overhead, Analyses, etc.	0.81	0.36	0.25
Total	4.00	2.65	1.50

*The cost for reagents in the flotation process is on the order of $0.15/ton.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

The application and advantages or disadvantages of flotation to the processing of hazardous materials is difficult to assess on a general basis. It probably would not be too difficult to make some judgments about the usefulness of flotation for any specific hazardous waste problem.

In general, however, if the process can be successfully applied, it could have advantages since it would be easy to apply using conventional and standard equipment.

The application of flotation to hazardous materials would most likely not include the extensive and costly crushing, sizing, and grinding steps involved in the conventional ore flotation process. Most hazardous materials for which flotation might be useful would probably be in the form of a slurry or solution which would go directly to conditioning and flotation. This would probably be a low cost and simple operation.

Nevertheless, it appears doubtful that the flotation process could be useful in any large way in handling hazardous materials since, in most cases, there are probably better and cheaper ways to handle the problem.

For example, many hazardous heavy metals in solution can be removed with simple lime treatment and settling. This is the common process around mineral processing plants that have trace amounts of such materials in effluent streams. Other heavy metals, for example, mercury, can be removed by sulfide precipitation. In any event, there is no reason to consider flotation, whose real advantage is in separating one solid from another. In cases where hazardous solids may be in suspension in a slurry, the preferred process would likely be simple flocculation and settling rather than flotation.

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B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD

1. D.W. Fursteneau, Univ. of Calif., Berkeley, CA.

2. Frank F. Aplan, Penn. State Univ., Univ. Park, PA.

3. S.T. Michaelson, Kennecott Copper Co., Salt Lake City, Utah.

FREEZE CRYSTALLIZATION

Prepared by

Joseph P. Tratnyek

I. CONCLUSIONS AND RECOMMENDATIONS

Freeze crystallization has been developed and used for desalination of water. However, it has never become a commercial operation. Presently, AVCO of Wilmington, Massachusetts has the only freeze crystallization installation in operation. AVCO has demonstrated in the laboratory that freeze crystallization can be used to process selected industrial waste streams, and interest is high to develop the process for this application.

The freeze crystallization technique can be used on liquid waste streams containing potentially hazardous materials in the order of 1-10% total dissolved solids (TDS). Output streams will have concentrations of 0.1-0.01% TDS and contaminants will appear in the product water in the same ratio as they appeared in the feedstock.

As the freeze crystallization process is developed for waste treatment, we see it becoming a viable technique for separating feed streams into a reusable or dischargeable water stream; and a solid stream which can be reclaimed, destroyed, or land-filled.

However, freeze crystallization for waste treatment remains experimental, and probably will remain so for several years as experience develops in this area. We recommend that it be considered for waste treatment where appropriate, with the recognition that it still is in the experimental development stage.

II. PROCESS DESCRIPTION

A. BACKGROUND

With the increased worldwide demand for fresh water for domestic and industrial use, various means have emerged for tapping the greatest source of water, the oceans. The oceans hold about 97% of the earth's water. Unfortunately, this water cannot be used directly, but must be made "fresh" by removal of salts (3.5% TDS or 35,000 ppm mostly as NaCl). So-called fresh water, or potable water, is water with no more than 0.05% TDS or 500 ppm dissolved salts.

Freeze crystallization has been proposed and tested for desalination of waters in several countries, notably, the United States, the United Kingdom, and Israel. Work in this area began in 1952 when the Office of Saline Water (OSW) was created by Congress with an initial budget of $42 million for economical processes for desalination. Work on freezing techniques appeared to have reached a high point in the mid to late 1960's. Although demonstration plants easily produced salinities less than 500 ppm TDS, and in many cases below 100 ppm, interest has generally waned because of economic considerations. U.S. companies such as Carrier, Colt, Struthers, Koppers, Rocketdyne, and AVCO have been associated with freeze crystallization development. Government support for these projects has provided the impetus for development. In recent years this impetus has waned with a decrease in funding. Only AVCO's Wrightsville Beach test facility remains in operation under the Office of Water Research and Technology (OWRT) which assumed OSW's responsibilities. Even continued operation of the Wrightsville Beach plant is in jeopardy of being terminated.

Although freeze processes for desalination of sea and brackish waters have been demonstrated, none have become commercial processes. Freeze desalination processes compete in development with solar evaporation, conventional multiflash evaporation, extraction, hyperfiltration or reverse osmosis, ion exchange, and electrodialysis. For desalting, only the evaporation processes and freezing are considered viable, and cost estimates by Colt and AVCO have shown lower energy costs for freezing. In spite of this, multistage flash evaporation has remained the standard desalting process.

Because of a lack of commercial interest in freeze desalination, attention is focussing on the use of freeze crystallization for processing streams other than salt water. AVCO has successfully demonstrated waste stream treatment with their Crystalex® process, thus broadening the potential applications for freeze crystallization processes.

B. UNDERLYING PRINCIPLES

When an aqueous solution containing dissolved salts is frozen, "fresh" water ice crystals form and the salts are concentrated in the remaining brine solution. The ice crystals can be separated from the brine by mechanical means, washed, and melted to yield fresh water (Refs. 1, 2). The remaining brine may contain potentially hazardous substances which can be treated further or disposed of. The freezing process resembles the distillation process in that heat transfer is a very important element of the process, and a change of phase is involved.

With a suitable means of separating the ice crystals from the mother liquor, freezing can be made into a process which yields a concentrated waste product stream and high-quality water (99+% pure). Since most of the developments in freeze crystallization have related to aqueous streams, our descriptions will refer mostly to ice. Theoretically, at least, these processes can be applied to nonaqueous streams as well.

C. OPERATING CHARACTERISTICS

Operating information is derived primarily for sea water and brackish feeds entering the freeze crystallization units (Refs. 3-7). A mathematical model for the freeze crystallization process applied to ice-brine systems has been developed by Wey and Estrin (Ref. 8). The freezing process is described and compared in general terms to other desalination operations by Probstein (Ref. 9).

Input salt waters normally contain about 3.5% TDS (35,000 ppm), mostly as dissolved salts. Basic purity of output water is 50-100 ppm as NaCl. At this level, other minor contaminants remain in the same ratios as present in the original feedwater. Greater purity of water is limited by the ice crystal wash procedure. From a practical point of view, the process becomes uneconomical if washing of ice crystals is carried out to get salinities as low as 1-2 ppm. At 20 ppm, the process is on the borderline of becoming economical. Problems may arise if freezing point depression, or if precipitation is encountered since both induce carryover of contaminants in the order of 300-500 ppm into the product water. Feedwater does not normally require pretreatment unless extreme pH is encountered (less than 2, greater than 12).

Problems involved in the freezing processes include handling and separating the ice-brine slurry and washing the ice crystals free of salts. The use of direct contact heat exchange and the low operating temperature encountered in freezing processes greatly minimize the problems associated with scale formation and corrosion.

Although the process is generally considered as a demineralization technique, it is capable of removing organic materials from water as well.

Freeze crystallization involves the following steps:

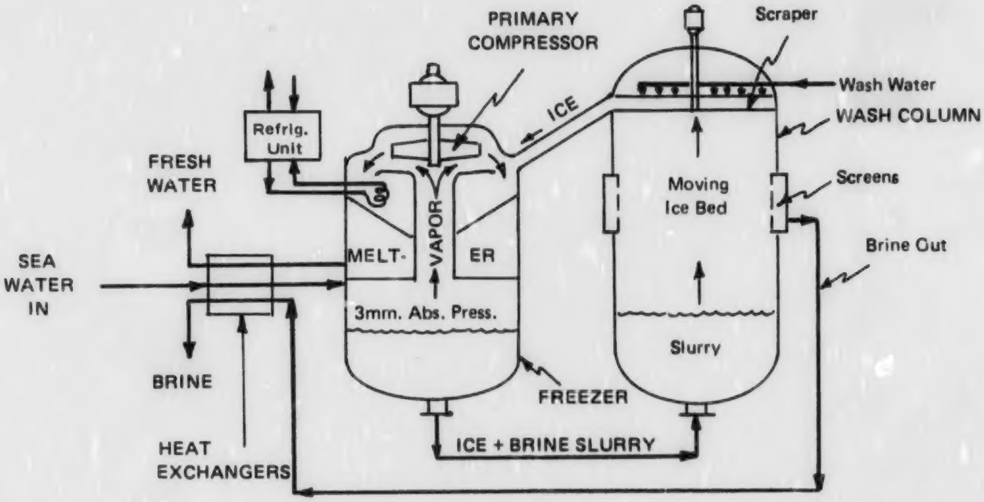
- heat exchange
- freezing
- washing
- melting
- refrigerant or energy recovery

There are basically two forms of the freezing process:

1. Vacuum flash/vapor compression (VFVC) in which water itself is the refrigerant, and

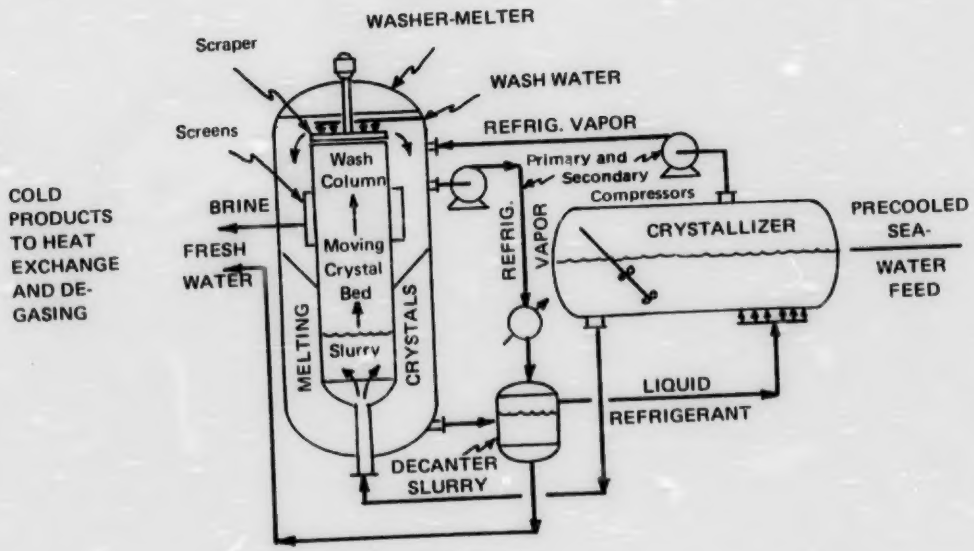
2. Secondary refrigerant freezing (SRF) in which butane or a halogenated hydrocarbon such as Freon is the refrigerant.

Barduhn (Ref. 10) and others (Refs. 1, 2) have reviewed these processes. Several variations have been proposed and demonstrated. Most closely associated with the VFVC has been Colt Industries; most closely associated with the SRF system has been AVCO Systems and University Engineers Inc. Diagrammatically, the VFVC and SRF processes are shown in Figures 1 and 2.


PRIMARY
COMPRESSOR
Scraper
Wash Water
WASH COLUMN
ICE
Refrig.
Unit
FRESH
WATER
Screens
Moving
Ice Bed
VAPOR
MELT-
ER
Brine Out
SEA
WATER
IN
3mm. Abs. Press.
Slurry
BRINE
FREEZER
HEAT
EXCHANGERS
ICE + BRINE SLURRY

Source: Ref. 10.

FIGURE 1 VACUUM FLASH DIRECT FREEZING PROCESS


WASHER-MELTER
Scraper
WASH WATER
Screens
REFRIG. VAPOR
Primary and
Secondary
Compressors
Wash
Column
Moving
Crystal
Bed
Slurry
MELTING
CRYSTALS
COLD
PRODUCTS
TO HEAT
EXCHANGE
AND DE-
GASING
BRINE
FRESH
WATER
REFRIG.
VAPOR
CRYSTALLIZER
PRECOOLED
SEA-
WATER
FEED
LIQUID
REFRIGERANT
DECANTER
SLURRY

Source: Ref. 10.

FIGURE 2 HYDRATE PROCESS AND FREEZING PROCESS WITH SECONDARY REFRIGERANT

1. Vacuum Flash/Vapor Compression (VFVC) Process

The VFVC operates at reduced pressure (3 mm absolute) which is below the triple point pressure of salt water where water is evaporated and ice is formed simultaneously. The water vapor is compressed to about 5 mm and is condensed onto the ice after it is freed of brine.

2. Secondary Refrigerant Freezing (SRF) Process

In the SRF system, pre-cooled salt water comes into direct contact with an evaporating refrigerant, such as butane or Freon, whereupon ice particles form. The ice-brine slurry produced is pumped to a wash column in which the bed of moving crystals is washed counter-currently by the fresh water product thus yielding brine-free ice. The clean ice is melted using the heat of condensation of the compressed refrigerant. The SRF system may be designed with multiple stage crystallization in order to improve purity and gain certain economic advantages.

3. E-C Process (Exchange Crystallization)

Lott and Sliepcevich (Ref. 11) at University Engineers have demonstrated a modification of the SRF system for desalination using high pressure (3000 psi) and a frozen liquid organic compound (kerosene) as the direct contact refrigerant. The process depends upon the inversion of melting points of water and refrigerant under applied pressure. The basic process is described by Cheng and Cheng (Ref. 12). This process has been designated the Exchange Crystallization process (E-C).

A demonstration plant, now inoperative, having a design capacity for producing 75,000 gpd of potable water from 150,000 gpd of sea water has been built and operated using this principle. The successful operation of this process depends on energy exchange engines (patented) developed by Cheng, Sliepcevich, and Lott. The exchange engine permits about 95% recovery of pressure energy used to pump the ice slurry.

4. Other Processes

Letan (Ref. 13) describes a direct contact cooled crystallizer in which the crystallized aqueous solution is fed downward through a specially designed column. It flows downward counter-currently to an organic coolant (chilled kerosene) injected at the bottom. The cold suspension of crystals and saturated solution is obtained at the bottom and further processed. Although this unit is intended primarily to crystallize organic salts it may be adapted to organic liquids, in which case the coolant has to be brine or water.

Recent interest has centered on eutectic freezing. Barduhn and Lee (Ref. 14) have recently reviewed the eutectic process and Schroeder has proposed operational designs (Ref. 15). In eutectic freezing the temperature is lowered to a point where both ice and salts precipitate simultaneously (the eutectic temperature). The freezing process thus has the added dimension to produce solid salt and fresh water, not just brine and fresh water. AVCO has been investigating eutectic freezing as a treatment process, and Fluor Corporation was awarded a contract to develop a conceptual design for a eutectic freezing plant.

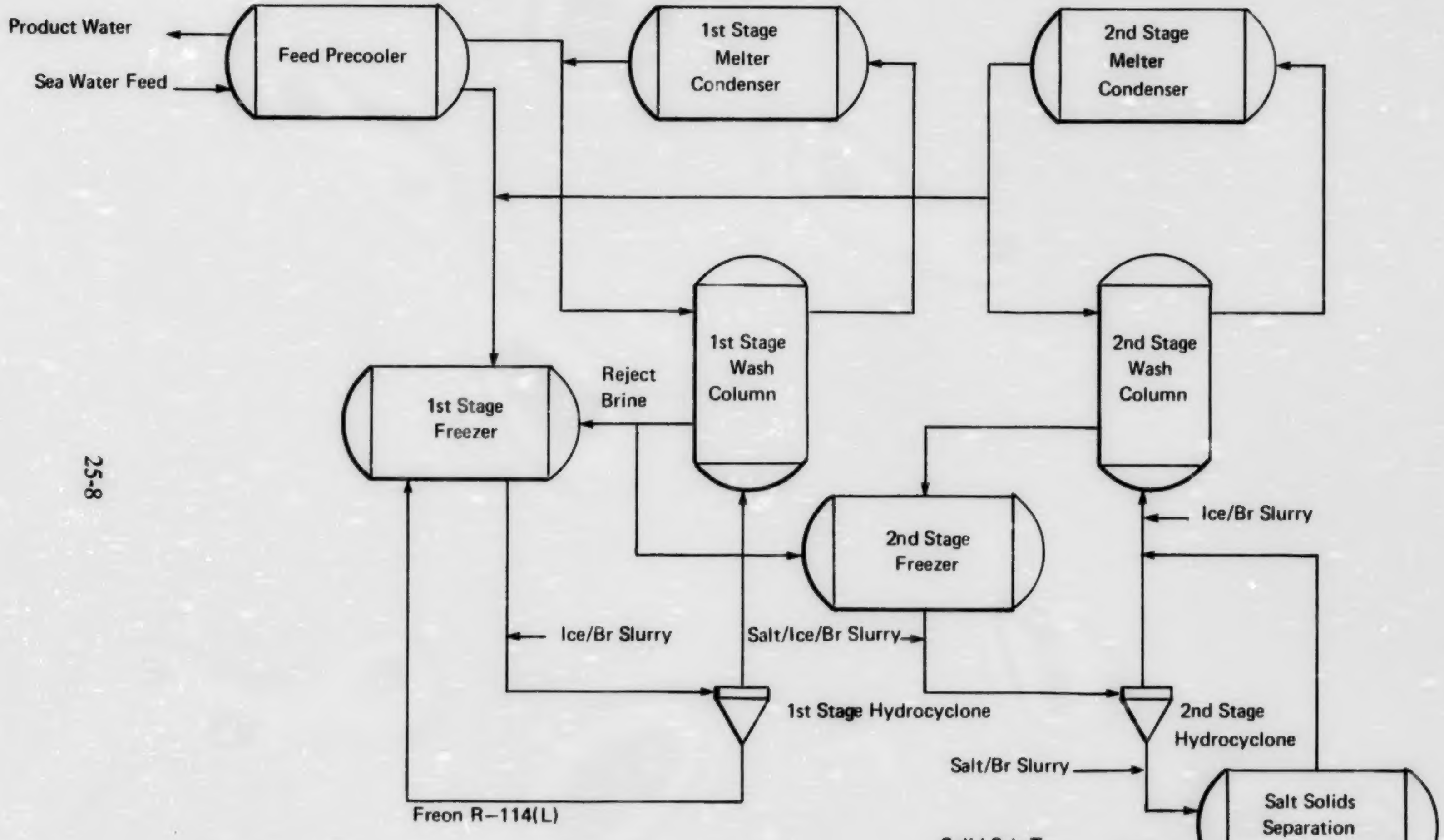
Figures 3 and 4 describe two conceptual designs according to Fluor Corporation. The AVCO design in Figure 3 is based on the use of AVCO's present Crystalex® process (to be described in detail in the next section) with additional equipment to achieve eutectic freezing. The Fluor design in Figure 4 is based on a single-stage concept.

In general brine is cooled to its eutectic temperature (-21°F) by direct contact with a liquid refrigerant at an operating pressure of about 5 psi. During cooling, ice forms, brine becomes more saline, and the freezing point drops. The temperature continues to fall along the freezing point depression curve until -21°F is obtained, whereupon the brine is 23% and is saturated with respect to NaCl. Further cooling causes precipitation as the solid dihydrate and as additional ice. Separation and additional treatment, filtration and drying, results in a solid product.

D. EQUIPMENT AND MATERIALS

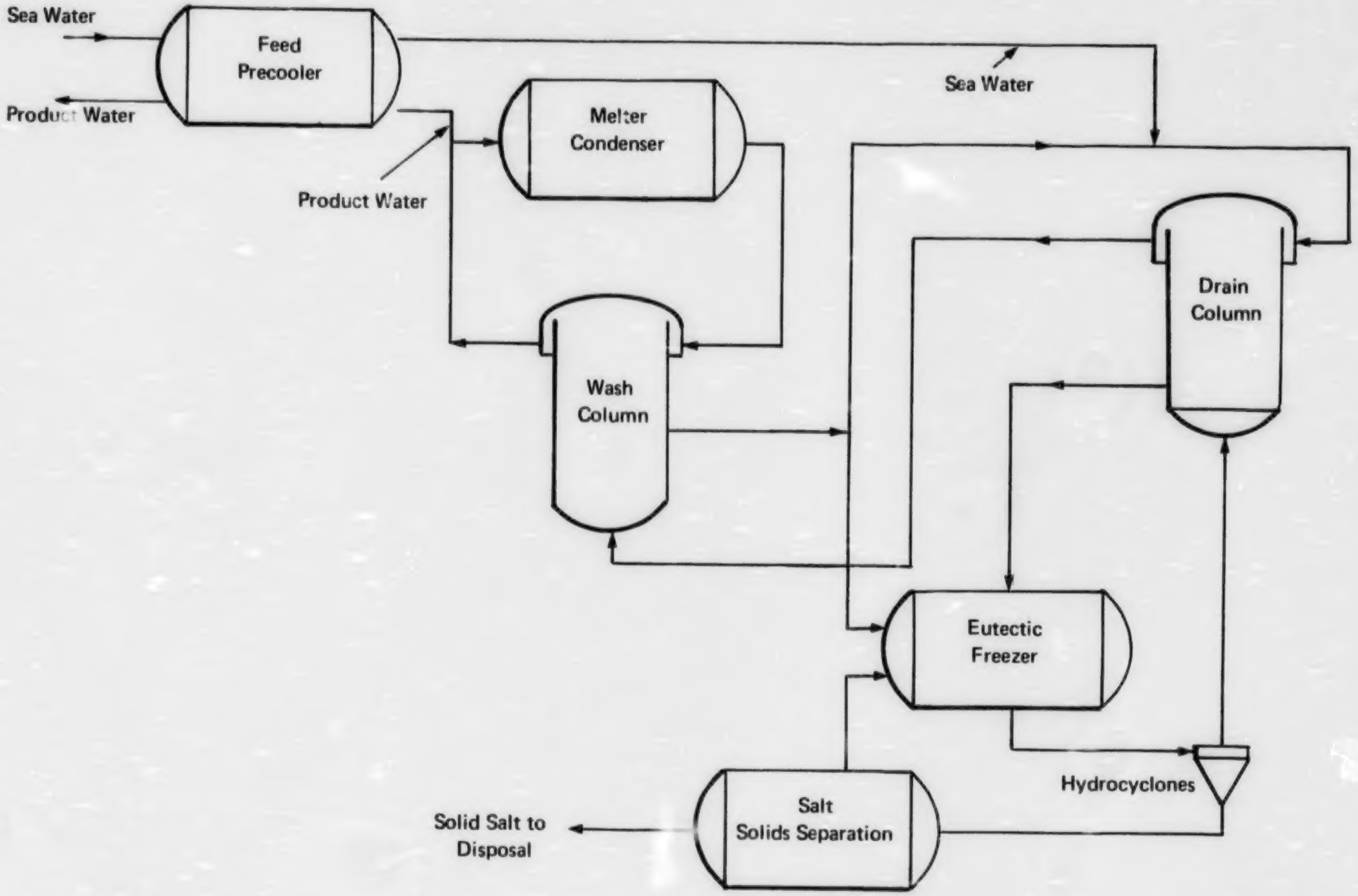
As stated previously, AVCO has the only freeze crystallization equipment in operation at this time. Their 75,000 gpd demonstration unit is operating on salt water at Wrightsville Beach, North Carolina. AVCO has a mobile unit capable of processing 1000 gpd and a laboratory experimental unit for 500 gpd. The AVCO process is called the Crystalex® process and will be described in detail here to illustrate equipment and operation. Data are taken from information supplied by AVCO Systems Division, Wilmington, Massachusetts (Refs. 7, 16-18). Some features of the process have been patented while others are pending. A detailed schematic is shown in Figure 5.

Referring to Figure 5, the Crystalex® process operation is as follows: The entering feed water is cooled by the outgoing concentrate and pure water. This cooled feed now moves to the freezer where it mixes with a refrigerant. Operation at low pressure causes the nonflammable refrigerant to boil and evaporate. Heat is extracted from the feed, yielding pure ice crystals and a concentrated solution of feed. The crystals, together with the concentrate, form a slurry which is pumped to the pressurized wash column. The ice forms a porous plug which is propelled upward by the concentrate flow through the plug, the concentrate leaving through screens in the side of the column. Concentrate which adheres to the ice crystals is washed off with a small amount of previously purified product water flowing from the top of the wash column through the screens. Ice is harvested by a revolving scraper at the top of the wash column, slurried, and pumped to the melter/condenser. Here, the evaporated refrigerant gas, which has been compressed, condenses on the outside of the


Product Water
Sea Water Feed
Feed Precooler
1st Stage Melter Condenser
2nd Stage Melter Condenser
1st Stage Wash Column
2nd Stage Wash Column
Reject Brine
1st Stage Freezer
2nd Stage Freezer
Ice/Br Slurry
Salt/Ice/Br Slurry
Ice/Br Slurry
1st Stage Hydrocyclone
2nd Stage Hydrocyclone
Salt/Br Slurry
Freon R–114(L)
Salt Solids Separation
Solid Salt To Disposal

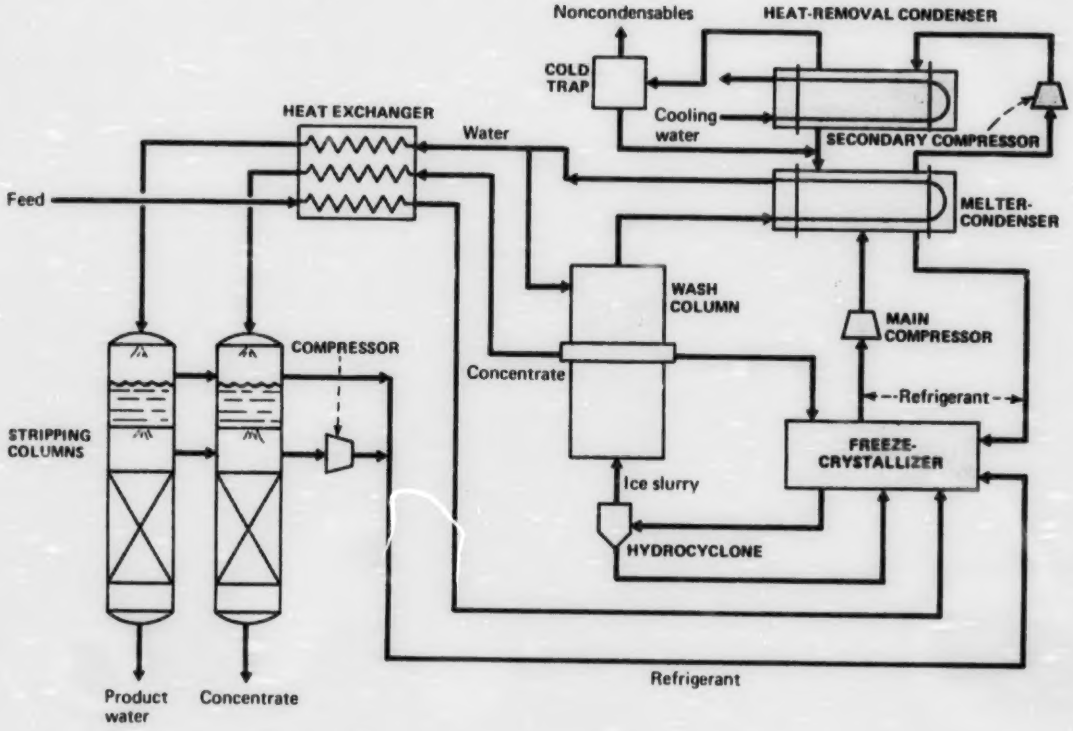
Source: Ref. 15.

FIGURE 3 CONCEPUTAL DESIGN FOR A 10,000-GPD TWO-STAGE EUTECTIC-FREEZING PILOT PLANT AS PROPOSED BY AVCO


Sea Water
Product Water
Feed
Precooler
Melter
Condenser
Product Water
Sea Water
Wash
Column
Drain
Column
Eutectic
Freezer
Hydrocyclones
Solid Salt to
Disposal
Salt
Solids Separation

Source: Ref. 15.

FIGURE 4 CONCEPTUAL DESIGN FOR A 10,000-GPD SINGLE-STAGE EUTECTIC-FREEZING PLOT PLAN


Noncondensables
HEAT-REMOVAL CONDENSER
COLD TRAP
Cooling water
SECONDARY COMPRESSOR
HEAT EXCHANGER
Water
Feed
MELTER-CONDENSER
WASH COLUMN
MAIN COMPRESSOR
COMPRESSOR
Concentrate
--Refrigerant--
STRIPPING COLUMNS
FREEZE-CRYSTALLIZER
Ice slurry
HYDROCYCLONE
Refrigerant
Product water
Concentrate

Source: Ref. 17.

FIGURE 5 CONTINUOUS FREEZE CRYSTALLIZATION PROCESS (CRYSTALEX®)

tubes, and is returned to the freezer. The ice slurry from the wash column is melted inside the tubes to yield pure water. This method prevents contamination of the water by volatiles. The fresh water from the melter/condenser, and the concentrate exiting from the wash column screens, return through the heat exchanger where, together, they cool the incoming feed water. The strippers remove almost all residual refrigerant remaining in the water.

Modification can be made to include two-stage freezing. The Crystalex® process is reported to be applicable to waste treatment with application engineering and equipment modification. As pointed out earlier, prior treatment is not necessary except in certain instances. Freon 114 is the refrigerant and only material required. Mild steel or aluminum are primary construction materials. Other details about equipment and components of the Crystalex® unit are described elsewhere (Ref. 18).

III. APPLICATION TO DATE

A. PRINCIPAL CURRENT APPLICATIONS

The freeze crystallization processes were originally developed for desalination but none have become commercial in the United States. Its present status is well described in Barduhn's paper (Ref. 10). Of the various units modelled and tested, only AVCO's Crystalex® plant is currently operational. University Engineers' E-C unit is intact, but operation ceased in December 1975. Although the need for potable water remains, large-scale operations for desalination have lost appeal, and other uses for freeze desalination are being proposed and investigated.

Desalination by freeze crystallization essentially reduces 3.5% TDS salt water (35,000 ppm) to less than 0.05% TDS (500 ppm) which is classified as potable. In practice freeze units will achieve 100 ppm readily. Freeze units will attain lower concentrations, theoretically 1-2 ppm dissolved salts in product water, but with great difficulty and much added expense. Efficiency drops off rapidly since ice crystals cannot be adequately washed to reduce impurity concentration to these lower limits. Since potable water has been the desired product, 50-100 ppm dissolved salt has been considered an acceptable achievement. Brine resulting from processing represents another disposal problem. There is no large-scale experience with streams other than sea water or brackish water.

However, Barduhn proposed treatment of sewage sludge at eutectic temperatures in 1963 (Ref. 14). Tests in 1964 and 1965 at −22°C were unsuccessful because solutions become very viscous (nearly glassy) so that complete crystallization became impossible. Dissolved inorganics at this point amounted to about 25% by weight and organics, about 4% by weight. Since then, AVCO has actively pursued treatment of industrial wastes in order to convert the Crystalex® process from a stagnant desalination process to one with broader commercial application. Experiments have been conducted on a small scale with varying degrees of success using AVCO's laboratory freeze unit on industrial wastes (Refs. 19-22). In order to make the Crystalex® process more effective for waste treatment, a second stage freezer, the Concentrex™ Process, has been added (Ref. 23), and eutectic freezing has been proposed.

The following have been tested by AVCO with some degree of success.

- sulfite liquor
- kraft liquor
- paper mill bleach
- solution containing acetic acid, methanol and aromatic acids
- metal finishing wastes containing heavy metals
- arsenal redwater

As an example, typical pilot plant results from plating rinsewater (Ref. 20) from pilot plant studies are shown in Table 1.

TABLE 1

PILOT PLANT RESULTS FROM PLATING RINSEWATER

Contaminant	Feedwater Concentration mg/l	Product Water Concentration mg/l	Percent Removal
Nickel	105	0.44	99.58
Cadmium	105	0.40	99.62
Chromium	110	0.225	99.80
Zinc	100	0.34	99.66
NaCl	30,000	120	99.60

Notes. Capacity of the pilot plant, 2500 gpd. Purity of final product water is controlled primarily by the length of the washing zone in the counterwasher and, to a lesser extent, by the quantity of washwater used.

Source: Ref. 20.

Other reports show purification of water in the following levels from indicated waste streams (Table 2). Note that product waters contain 120 ppm or greater total of initial contaminants.

The Dutch refrigeration specialists, Grenco, which is part of the Grasso engineering group, claimed they are able to produce water containing only 10 ppm impurities from a wide variety of sources without any of the serious drawbacks which have held up commercial exploitation of freeze concentration as a process technique (Ref. 24). Their apparatus consists of a three-stage process which achieves total ice/mother liquor separation by a special crystallization process in order to reduce product entrainment in the final "pure" water. This unit is reported to be available as a commercial plant (250 kg/h). Grenco's process is aimed at removal of water from feedstock fluids. It is not known if their units are now in operation.

Baker (Ref. 25) has investigated trace organic contaminant concentrations by single-stage freeze concentration at −12°C from synthetic laboratory solutions and various tap waters. Organic recovery was reduced as ionic strength of solutions increased. For a specific operation prediction of organic recovery versus initial total dissolved salt content could be made. Organic chemicals originally included phenols, substituted phenols, volatile fatty acids and acetophenone. About 90% recovery of 1 ppm m-cresol in solutions containing 100-300 ppm dissolved salts was possible.

Sabdell (Ref. 26) reviews freezing and eutectic freezing in relation to removal of heavy metals from water.

TABLE 2

RESULTS FROM INDUSTRIAL WASTE TESTS

Solution		Composition (mg/l)	
		Feed	Product
Cooling Tower Blowdown #1	Na	70	3
	SiO_2	90	22
	Mg	150	5
	Cl	150	28
	Ca	320	14
	SO_4	600	31
	TS	2,700	130
#2	TDS	24,000	150
Electronics Plant Waste	Na	300	6
	Cl	430	9
	Ca	790	110
	SO_4	2,800	280
	TS	4,700	460
Waste Salt Solution	Mg	2,000	
	Co_3	2,000	
	Na	11,000	
	Cl	18,000	
	TDS	33,000	150
Ammonium Nitrate Waste	Ca	3,000	
	NH_3	12,000	
	NO_3	56,000	
	TDS	71,000	300
Weak Sulfuric Acid Waste	TDS	5,000	250
Hot Caustic Extract (from pulp mill)	TDS	46,000	150

Source: Ref. 22.

C. POTENTIAL APPLICATION TO WASTE TREATMENT

Freeze crystallization appears to have potential application to treatment of hazardous wastes. In effect, demonstrations have been made on inorganic and organic species in solution as indicated in the previous section. It must be remembered that freeze crystallization works on liquid streams. The upper solids concentration level will be governed by viscosity requirements within the system. The highest concentration feed stream thus far investigated is in the order of 10% TDS. Salt water is about 3.5% TDS. Streams down to about 0.003% TDS have been studied in the laboratory. The low level streams probably would require a concentration step prior to freezing. Because freezing is just emerging as a means of treating waste, operational data are minimal.

Freeze crystallization processes may be used in low-viscosity liquids, slurries, and sludges. Still bottoms will not be processable. The input stream must have a component that freezes. Industrial waste effluent always consists of multicomponent solutions whose freezing point depression and operation characteristics for various levels of dissolved and solid concentration can be determined both analytically and experimentally.

In many cases, industrial wastes may contain suspended solids or may be saturated with respect to one or more dissolved salts. The dissolved solids will precipitate as the concentration of the waste solution is increased in the crystallizer. All typical hazardous components such as dissolved heavy metal cations and anions, cyanides, and organics are theoretically treatable by freezing. Mixed inorganic/organic solutions may be treatable.

Two products are likely to result from a freeze processing – a liquid stream and a brine-like or wet solid stream. The liquid stream is normally water which may be recyclable or useable depending on residual contamination. It also may be an organic solvent. The brine or solid will normally contain the concentrated hazardous ingredients which then must be disposed of in some other manner.

Practical demonstrations have shown that aqueous waste streams with as little as 30 ppm total dissolved solids can be treated by freeze crystallization with removal of 99.9% of contaminant. All dissolved contaminants will be reduced in the same ratio, regardless of their initial concentrations. Treatment of fully organic streams by freeze crystallization has not been attempted.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

The main competition to freezing processes are evaporation/distillation processes. For desalination and, potentially, for waste treatment, energy costs are reported less for the freeze processes.

For a single-stage freeze concentrator, energy (electrical) required is in the order of 60 kWh/1000 gal of product water, and for a two-stage unit, 75 kWh/1000 gal of product water. No heat or steam is required. Barduhn (Ref. 10) compares the energy usage of sea water desalting processes in terms of total required energy as gallons of oil needed per 1000 gal of fresh water produced. The most important presently used evaporation process, multi-stage flash, now requires 7 gallons of oil/1000 gal water; projected use is less than 5 gallons. Freezing now requires 3 gallons of oil/1000 gal water. Sliepcevich claims that because of energy recovery in the E-C system, energy requirements are about 20% lower than the AVCO process presently in operation. Schroeder at Fluor Corporation proposes to couple freeze desalination to LNG plants in order to further save energy.

Although energy requirements may be considered high compared to membrane systems, they are lower than the now most widely used evaporative systems. Freeze crystallization can be considered moderately energy intensive. However, as energy costs rise, freeze energy costs will look more attractive.

B. ENVIRONMENTAL IMPACTS

Aside from electrical energy requirements and their indirect environmental considerations, only process emissions and product streams need to be considered for freeze crystallization processes.

Emissions would consist of some water vapor and non-condensables and refrigerant (e.g., butane, Freon, kerosene, etc.) which is lost in the process. Refrigerant loss is estimated to be about 1 ppm dissolved in water.

The product streams will consist of water, which if potable and free of toxic ions, can be consumed or returned to the environment. Product water which does not meet minimum discharge requirements can be recirculated and used within the industrial plant, or it must be treated further.

The largest impact on the environment will be related to the brine or solid product which will contain the majority of hazardous components. Disposal of brine represents a considerable problem. Wastes with considerable organic content may have significant energy value and could be burned. Toxic solids could be disposed of in land fills, or would require some subsequent detoxification step. Of considerable interest would be reuse or recycling the recovered dissolved solids.

C. ECONOMIC ANALYSIS

Many economic analyses of freeze crystallization have been made and can be found in the literature and OWRT. In 1973, AVCO published an analysis, now out of date, indicating a cost of about $2.00/1000 gal of water for a 100,000 gal plant (Ref. 27). Barduhn and Schroeder have conducted economic analyses which are favorable to freeze crystallization processes. Sliepcevich reports that a 5,000 gal/day plant would have a water production cost of $2.25-3.00/1000 gal/day. Costs will vary according to plant size, concentration of input and output, whether the unit is one or two stage, and operating conditions. A 75,000 gal/day single-stage freezer is compared to a two-stage unit as follows:

	Single-Stage	Two-Stage
	(thousands of dollars)	
Capital Cost	$600	$800
Installation Cost	60	80
Energy	60 kWh/1000 gal	75 kWh/ 1000 gal

Estimated costs developed at Arthur D. Little, Inc., based on one man/shift are given in Table 3. Based on interpretation of the cost figures, a working figure for freeze crystallization is assumed to be $6-12/1000 gal of product water. We have not attempted to place a value on potentially recoverable materials which would be credited against reducing operational costs.

It should be noted that freeze desalting coupled to LNG plant effluent (Fluor Corporation) is being proposed and studied as a means of effecting savings in capital, operating, and water costs. Cold seawater, near the freezing point, from the LNG plant could be utilized in a freeze desalting process. Conceivably, waste streams (50MGD) might replace seawater, and be processed, if they were available and if logistics could be handled.

Other advantages, inherent to freeze crystallization would result in cost savings. Because concentration takes place by the freezing of water in direct contact with the refrigerant, there is no heat-transfer surface or membrane to be fouled by the concentrate or other contaminants. Prior treatment of feed is unnecessary, even with waters normally presenting severe problems with other processes. Suspended solids do not affect the process and are removed only as required by the end use to be made of the recovered products.

TABLE 3

ESTIMATED OPERATING COSTS FOR FREEZE CRYSTALLIZATION

Basis: 50,000 Gal/Day – 350 Day/Yr Operation
Estimated Capital Investment $280,000

	Annual Quantity	Cost per Unit Quantity	Annual Costs
Variable Costs:			
Labor	18,500 hr	$12.00/hr	$102,000
Maintenance (4% of Inv.)			11,000
Electricity	16×10^6	0.02/kWh	32,000
Chemicals			1,000
Total Variable Costs			$146,000
Fixed Costs:			
Taxes & Insurance (2% of Inv.)			5,600
Capital Recovery (10% – 10 yrs)			45,400
Total Fixed Costs			$ 51,000
Total Costs			$197,000
Unit Costs ($/$10^3$ gal)			$ 11.56

Source: Arthur D. Little, Inc., estimates.

The low temperatures associated with the process minimize corrosion problems and allow inexpensive materials to be used in piping, pumps, and vessels. Thus, much of the cost associated with evaporative processes is avoided. A drawback to the reuse of water recovered by evaporative systems is that any volatile contaminants present in the feed will also be present in the recovered water. In freezing processes the volatiles are isolated from the washed product by tubes located in the melter/condenser.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Although freeze crystallization processes are not presently used for processing industrial wastes on a commercial level, it is likely that its use here will become a reality, even if only as a source of recyclable plant water. AVCO reports that it expects to have a viable waste treatment unit in operation within 1-2 years, and they are developing their outlook and research for their freeze operation in the direction of waste treatment.

Two-stage, and eutectic freezing appear to be the most useful freeze techniques that will be applied to waste streams. Aside from species noted in the text, natural and synthetic polymer containing solutions, and latices may be processable. The limiting factor will be the rheological properties of solutions at low temperatures. Foam, glassy, or viscous masses can not be freeze crystallized. Concentration limits and behavior of complex industrial streams will probably vary from one stream to another, which will require an analytical or test run to determine feasibility and operating parameters.

Input solutions in the order of 1-10% TDS probably will be most suitable for processing. Suspended solids may or may not complicate separations. Although, normally, prior processing is not required, concentration and/or filtration may be necessary on occasion. Aftertreatment will depend on the products produced and their disposal requirements.

The capacity and operating costs of a freezing recovery system are primarily functions of the total water flow and only to a limited extent dependent on initial waste concentrations in the feed stream. Thus, it is important to employ methods, such as countercurrent rinsing, which will reduce the total water flow.

Theoretically, the freeze crystallization process is capable of concentrating most all of the encountered hazardous materials in waste streams, although equipment changes may be required for handling and collecting products.

As regulatory bodies impose more constraints on industrial waste emissions and the cost of water rises, freeze crystallization processes will become more important when recycling is considered. Large capital costs will be balanced by recovery benefits and lower energy costs than found in the comparable widely used evaporation/distillation processes.

Although the interest in freeze processes is reviving, it has suffered because continuous large-scale operation has never been achieved over any significant length of time in order to obtain needed operational data. Water desalination demonstration units have come and gone; only AVCO's Crystalex® process is presently in operation. Its projected use for waste streams, in each case represents a new development program with uncertain operational characteristics.

Freeze crystallization has been demonstrated for desalination and, in the laboratory, for waste processing. However, encouraging the progress of this work, further development is indicated.

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B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN FIELD

28. Harold E. Davis, Program Development Manager, Water Purification Program, AVCO Corporation, AVCO Systems Division, Wilmington, Massachusetts.

29. James W. Ryan, Manager of Operations, Stokes Division, Pennwalt Corporation, Philadelphia, Pennsylvania.

30. Allan J. Barduhn, Professor of Chemical Engineering, Syracuse University, Syracuse, New York.

31. Paul J. Schroeder, Fluor Corporation, Anaheim, California.

32. Cedomir (Cheddy) M. Sliepcevich, Professor of Chemical Engineering, University of Oklahoma, and University Engineers Inc., Norman, Oklahoma.

33. Jerry L. Lott, University Engineers, Norman, Oklahoma.

34. Joseph J. Strobel, formerly Assistant Director OSW, OWRT, Washington, D.C.

FREEZE DRYING
(LYOPHILIZATION)

Prepared by

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I. CONCLUSIONS AND RECOMMENDATIONS

Freeze drying (lyophilization) is a process in which water vapor is sublimed from a sample containing frozen water in a high-vacuum system, thus being in effect, a drying operation. Its commercial use includes freeze drying of coffee and other foods as well as pharmaceuticals. Although sublimation in vacuum is theoretically applicable to non-aqueous systems, lyophilization is the only commercial application of freeze drying.

No waste streams are presently treated by freeze drying; in fact, freeze drying of foods faces a lukewarm future. Energy consumption for refrigeration and vacuum requirements is high, and the process is batchwise and very slow.

Accordingly, there is little industrial interest in development of freeze drying for other applications. We recommend no further support for its use in waste treatment applications.

II. PROCESS DESCRIPTION

A. BACKGROUND AND OPERATING CHARACTERISTICS

Freeze drying is a concentration process which relies on a refrigeration cycle with vacuum (Refs. 1-5). At temperatures below 0°C, water is removed by sublimation as long as the partial pressure of moisture in the gas phase over the sample is less than the vapor pressure of water in the sample. The drying operation usually proceeds in two stages. In the first, most of the water as ice is sublimed from the frozen sample in a high-vacuum system. The temperature is kept well below 0°C. In the second stage, the nearly dry product is dried at a higher temperature, depending on stability, in order to attain a minimum moisture level in the shortest time. Removal of water vapor under high vacuum must be efficient to maintain low vapor pressure in the system. Three methods generally employed are (1) condensation and refreezing at a temperature below that of the sample, (2) absorption on a desiccant, and (3) direct pumping. General principles, with emphasis on industrial applications, have been described by Flosdorf (Ref. 6).

B. EQUIPMENT AND MATERIALS

The basic equipment comprises a sample chamber, a refrigeration system, and a vacuum system. The size of commercial freeze-dryer chambers ranges from 500-2000 ft^2 of evaporator surface area. In recent years the trend has been to 1000 ft^2 chambers which represent an optimum size in terms of flexibility, downtime, pumping requirements, materials handling, maintenance, and overall economy. Aside from relatively small units built for the pharmaceutical industry which are of standard construction, most large units are custom engineered.

Utility requirements for refrigeration and vacuum equipment are high and the process is fairly labor-intensive. Pumping times of 6-12 hours at -10 to -60°C and 100 to 750 microns of pressure are not uncommon. Since units must be loosely loaded for efficient water removal, throughput/cycle is low. On occasion, a load may require 96 hours/cycle to remove only a few liters of water. Because of high-processing costs, freeze drying manufacturers would not recommend freeze drying for waste processing.

III. APPLICATIONS TO DATE

A. PRINCIPAL CURRENT APPLICATIONS

Freeze drying is valuable for drying unstable materials, since water is removed at low temperature. It is currently used industrially, primarily in the food processing and pharmaceutical industries. The greatest use of freeze drying is in preparation of freeze-dried coffee. It is also used to prepare fruits, vegetables, meats, and seafoods. Penicillin, veterinary, and biological products are routinely processed by freeze drying. A list of U.S. patents issued to Stokes Div., Pennwalt Corp. gives some indication of the scope of the freeze-drying process (Sect. VI B).

B. POTENTIAL APPLICATIONS TO WASTE TREATMENT

There is no known current use of freeze drying to process waste streams. Freeze drying was once studied to concentrate residual metals in ppb by removal of water from sludges, but a practical process did not result. Freeze dry equipment manufacturers have reported inquiries into use of freeze drying for waste management, mostly waste water sludges, but action has not materialized. Cost of equipment and high energy costs have prohibited use on wastes. In fact, the food industry has begun to move away from freeze drying as uneconomical (Ref. 7). Furthermore, presence of non-drying or hygroscopic materials in waste would preclude effective drying.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

Freeze drying is an energy-intensive operation and results in low batch yields. Operational and equipment costs are high. The cost of a large unit which might process pounds of material/hour would conservatively cost $300-500K. Freeze dry equipment manufacturers do not recommend its use for waste treatment.

The increased price of energy makes freeze drying an even more expensive way to remove water. Instant coffee, the only major volume product used now costs about 30-50% more than spray drying.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Freeze drying holds little promise for waste separation on a commercial scale. It is limited to batch operation and is slow and costly. It is essentially a dehydration process. Dehydration of waste can be achieved more effectively by other means such as spray drying.

Although work is being done by King at the University of California; Ma. Pletre, and Arsem at Worcester Polytechnic Institute; and the Pacific Geothermal Food Desiccation Research Institute (Ref. 7) to reduce energy use, and others are working to improve heat transfer and cycling time (Refs. 8, 9), freezing drying will remain an expensive desiccation operation if applied to wastes. The residual solid will still require disposal or treatment. Of course, if freeze drying could lead to a high value recyclable product from a waste stream, its use could not be excluded.

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B. PATENTS

U.S. Patent No.	Subject
2,215,265	Concentration and Preservation of Food Products and Biological Substances
2,345,548	Process of Freeze-Drying by Direct Pumping
2,380,036	Desiccation of Citrus Fruit Juices
2,396,561	Process of Freeze-Drying Involving Transfer of Hot Materials
2,400,748	Process and Product of Dehydrating Foodstuffs
2,471,677	Process of Desiccating Orange Juice Involving Freeze-Drying

U.S. Patent No.	Subject
2,471,678	Process of Desiccating Lemon and Lime Juices
2,509,681	Process of Desiccating Fruit Juices and Other Beverages
2,513,991	Process for the Desiccation of Aqueous Materials from the Frozen State
2,577,704	Process of Drying Plums and Grapes
2,602,825	Sublimation, Condensation, and Recovery of Solid Materials
2,605,554	Process for the Desiccation of Labile Aqueous Materials
2,608,472	Rotary Type Sublimation Apparatus
2,789,909	Process for Freeze-Drying Soft Cheese
3,022,619	Vacuum Stoppering Apparatus
3,135,589	Drying Apparatus Using Electrically Heated Shelves
3,145,562	Apparatus and Method for Ascertaining Optimum Drying Conditions
3,146,077	Freeze-Drying Using Radiant Heat
3,152,453	Apparatus and Method for Solidifying Liquid Particles
3,174,229	Continuous Drying Apparatus and Method
3,176,408	Freeze-Drying Apparatus Using Continuous Weighing
3,184,862	Apparatus for Drying Consisting of a Removable Cart with Tray-Supporting Shelves
3,230,633	Freeze-Drying Apparatus and Method for Shortening Cycles Times by Increasing Heat Transfer
3,233,334	Flash Drying Apparatus and Method Utilizing Intermittent Pulses of Drying Gas
3,238,638	Flow-Through Type Drying Apparatus
3,247,602	Ribbed Freeze-Drying Tray and Method of Manufacturing
3,261,110	Improved Ribbed Freeze-Drying Tray
3,264,747	Method and Apparatus for Continuous Freeze-Drying
3,264,756	Drying Tray
3,281,949	Freeze-Drying Apparatus and Method Using Internal Condenser

C. ORGANIZATIONS EXPERIENCED IN THE FIELD

1. Stokes Division, Pennwalt Corp., Philadelphia, PA.
2. The Virtis Co., Gardiner, NY
3. Vacudyne Altair, Chicago, IL
4. Alpha Electric Refrigeration Co., Detroit, MI
5. Ametek Inc. Process Systems, Durham, NC
6. Hull Corp., Hatboro, PA

FREEZING, SUSPENSION

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I. CONCLUSIONS AND RECOMMENDATIONS

We chose the term suspension freezing for a process in which the separation of suspended solids in a liquid can be aided by agglomeration of the solids by freezing. This process has been demonstrated in a limited way in the dewatering of alum sludges. Natural freezing or freezing by refrigeration and subsequent thawing of sheet or bulk sludge can be used. Freezing the sludge causes the suspended particles to agglomerate and form relatively large floc particles. Upon thawing, these floc particles separate rapidly leaving a clear supernatant and occupy significantly less volume than before freezing. The solids then can be separated by filtration or decantation and the residual water finally removed by natural drying or evaporation.

At present, there are no practical applications of freeze suspension in the United States. Given the present state of the art, it is unlikely that commercial processing equipment for freeze dewatering will be available within the next five years, although interest in the process will be maintained. Pending further developments in freeze processes for dewatering, we see no application at this time or the near future. If natural freezing cannot be utilized, then the method will be energy-intensive.

II. PROCESS DESCRIPTION

A. BACKGROUND

Suspension freezing, either by natural freezing or through refrigeration, has been proposed and investigated for treating sludges and gelatinous materials as early as 1940-1950 (Ref. 1). These, and recent investigations (Refs. 2-8) have been aimed primarily at dewatering municipal water plant sludges which are difficult to process. In order to permit handling and disposal of water treatment sludges, which can vary from 1-5% solids depending upon their source, concentration by dewatering is necessary.

Regulations preclude directly returning potentially hazardous sludges and waste solids to surface waters. Current practice is to dewater sludge by techniques which include gravity thickening in drying beds, vacuum filtration, filter pressing, and centrifugation. The concentrated solids are collected and placed in landfill. Water is processed and then returned to surface waters essentially free of organic and inorganic materials. Chemical pretreatments and use of filter aids may be used to hasten separation of solids. These treatments all suffer from inherent operational limitations so that an efficient treatment and disposal system is still needed.

Freeze dewatering has been proposed as a method which might even eliminate the need for chemical preconditioning treatment with alum, lime, and polymer, and might make separation of solid and water more economical.

B. UNDERLYING PRINCIPLES

The freezing point is the temperature at which a liquid becomes a solid. Suspension freezing may provide a freeze separation process in two ways.

(1) **Crystallization** – As a liquid mixture freezes, the solid that forms first usually has a different composition than the liquid, and formation of the solid changes the composition of the remaining liquid, usually in a way that steadily lowers the freezing point. This principle is used in purifying mixtures, successive melting and freezing gradually separating the components. This method is discussed elsewhere.

(2) **Freeze-conditioning** – Freezing of a sludge is directed towards accomplishing physical and mechanical changes in the suspended solids or gel particles, rather than crystallization of dissolved salts. Although crystallization of some soluble material may occur in the sludge, crystallization of water to ice is the mechanism utilized since sludge already contains solid particles of material. Although several mechanisms describe how freezing alters solid particles, the processes are complex and vary with the nature of the sludge and manner of freezing. It has been shown that freezing a sludge causes the suspended solids to agglomerate and form relatively large floc

> particles (Ref. 3). Upon thawing, these floc particles settle, leaving a clear supernatant and occupy significantly less volume than before freezing. Filterability is increased. The conditioning effect can be explained as the result of dehydration and pressure exerted on the sludge particles by the ice structure, thus causing agglomeration and densification (Ref. 9). This treatment was found to be effective on all types of sludges: primary, secondary, activated, and digested.

In spite of the recurrent interest in freeze dewatering, the literature is rather limited. Work and literature concerned with soil freezing and frost damage prevention are allied to sludge dewatering problems and have been drawn upon by workers in the field to develop sludge dewatering concepts (Ref. 10).

C. OPERATING CHARACTERISTICS, EQUIPMENT AND MATERIALS

Because most work in sludge dewatering has been conducted in the laboratory or only on a demonstration scale, reliable operating characteristic data is not available. For materials other than aqueous sludges, see Freeze Crystallization, Freeze Drying, and Zone Refining. Only waste water treatment plant sludges are known to have been subjected to suspension freezing. Proposed processes might involve additional conventional treatment plant operations (water treatment clarifiers, grit removal, centrifugation, polyectrolyte sludge thickening) prior to freezing and filtering. Freezing may be by natural freezing in holding ponds or containers, or by means of refrigeration. Critical factors are the nature of the sludge, time taken to freeze a sample, length of time a sample remains frozen, and percent of freezing. Freezing in bulk can require days. More recent attempts at sludge dewatering utilize fast freeze of films of sludge.

The freezing itself can be natural in northern climates and represents a slow process in large holding lagoons (Ref. 4). The process can be made more effective by spraying the sludge from a nozzle (Ref. 2). Snow cover on lagoons impedes freezing and requires removal for successful operation. In order to improve speed and gain control of the freezing operation, propositions have been made to freeze films of sludge on a cold surface through mechanized means (Refs. 2, 5). Direct slurry freezing in contact with a refrigerant (e.g., liquid butane) which is bubbled through the sludge are reported to enhance separation of sludge and water (Ref. 6).

In the case of natural outdoor freezing, the basic requirement is a lagoon or containment presenting a large surface area. Upon thawing, the water can be decanted and coalesced sludge filtered off or collected on screens. Film freezing and refrigerant freezing require apparatus which as yet has to be developed.

III. EXPERIENCE WITH PROCESS IN TREATING MATERIALS

A. HISTORY OF USE

As mentioned above, experience with freeze dewatering of sludge has been on a laboratory or demonstration level only. Work has been primarily on alum sludges, the type most commonly encountered in water treatment, and one most difficult to dewater.

Sludge dewatering experiments on sewage treatment plant sludges, aluminum hydroxide sludges, paper mill and water plant alum sludges, and phosphate sludges have been described (Refs. 2-5). The waste sludge arising from the activated sludge process is probably the most difficult to dewater, and large amounts of chemicals, such as ferric chloride, lime, organic polymers, etc., are used to condition sludge prior to dewatering. In order to eliminate the cost and need for chemical conditions, attention has been turned to physical methods, such as freezing. Laboratory experiments and some pilot demonstration work have progressed at the university level (University of Alaska, Kansas State University, and St. Louis University), and at the industrial level (Rex Chainbelt, Inc.). Demonstrations have been made by the City of Milwaukee. The EPA has sponsored projects in this area. However, at present, we know of no active commercial units in operation in the U.S. and no industrial waste treatment by freezing.

B. PRINCIPAL CURRENT APPLICATIONS

The only actual use of sludge freezing is in Winnipeg, Canada (Refs. 11-12) where it is employed as a mechanical aid to facilitate hauling of sludge. Note that it is not used for dewatering. Their operation has been in effect for about 15 years. It is claimed to have produced a 10-fold reduction in processing cost.

The City of Winnipeg pumps sludge (3%) from its secondary treatment sewage plant to drying beds during the warm season, where settling of solids and decantation of water builds sludge to about 10-12% solids. During winter, the sludge beds are allowed to freeze until they can support moving equipment, usually in January. The frozen mass (about 15-20% solids) is ripped and removed to stockpile or disposal on land. The material is not usually allowed to thaw or dewater, except that deep tanks filled with sludge during the winter months require a second freeze season to consolidate solids. Snow is removed to hasten freezing. Although sporadic attempts have been made to utilize this freeze process in other places, Winnipeg remains the only freeze operation.

C. POTENTIAL APPLICATIONS TO WASTE TREATMENT

Application of suspension freezing for the dewatering of other forms of waste has not been described. Although useful for concentration of metal hydroxides (Al, Fe, Ca, etc.) from aqueous sludges, its effectiveness for dissolved materials which may be present in addition has not been examined. Soluble, heavy metal ions and some organo-metallic compounds may be sorbed by the floc particles in the sludge. Suspension freezing may be a useful procedure to facilitate gross mechanical handling of suspended solids, but it is far from being controllable or an efficient technique for reliably removing potentially hazardous components. Hazardous components may remain both in the liquid and solid forms, and both will require further processing for management.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Although energy requirements for natural freezing in outdoor situations are very small, direct contact freezing via mechanical refrigeration or by direct contact with a refrigerant would require large energy expenditures. Rexnord, Inc., originally interested in commercial application of freeze dewatering back in 1970, abandoned interest at that time because they found it impractical (Ref. 13). For activated sludge treatment, capital and operational costs were estimated to be 6-8 times conventional treatment costs (ferric chloride treatment and filtration). Furthermore, space requirements were 150 times conventional. Since then, energy requirements has risen considerably and equipment development has been lacking.

B. ENVIRONMENTAL IMPACTS

Environmental impact would relate directly to the quality of water discharged back to surface water, the energy used to operate the plant, the degree of hazardous component retained by the sludge solids, and the means of disposing of the sludge solid. Since freeze suspension does not destroy the hazardous component, it will be retained by the solid or water, or may be distributed between them. Without further treatment or precautions, the two phases cannot be returned to the environment without imposing a threat by the toxic substance.

C. ECONOMIC ANALYSIS

Reliable current cost information is not available. The City of Winnipeg reported in 1973 that the operating cost of their natural freezing process was $0.95 per dry ton of sludge. Capital costs (about $600,000) which must be amortized include those for land, piping, and pumps. One can see that the investment, even without post-treatment, is large. Refrigeration requirements for an equivalent operation not based on natural freezing would obviously be high. Randall (Ref. 6) compares a butane-freezing process for activated sludge dewatering with other processes in his article published in 1975.

Process	Cost of Conditioning per Ton of Dry Solids with Variable % Solids (post treatment equipment costs not included)
Wet Air Oxidation (Zimpro Process)	$30-35
Heat Treatment (Porteaus Process)	8-20
Anaerobic Digestion	15-20
Aerobic Digestion	–
Chemical Conditioning	8-25
Freezing	6-30

Freezing by conventional refrigeration equipment has a high energy requirement while the slurry freezing method using butane proposed by Randall has a relatively low energy requirement. After-treatment is required for both. The advantages of refrigerant freeze processing based on crude economic data are not established to date.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Suspension freezing is a technique which has been demonstrated, mostly in the laboratory, for dewatering sewage plant sludge. Although economics of operation appear favorable in northern climates where natural freezing can occur outdoors, refrigeration techniques will be required in other areas where freezing will have to occur in process equipment. Actual process costs may be expected to be high in such circumstances. Equipment costs can also be expected to be high. At present, no equipment has been developed to process sludge by freeze techniques, and equipment development will lag until economic advantages can be proven.

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3. T.E. Osterkamp, Dept. of Physics and Geophysical Institute, University of Alaska, Fairbanks, Alaska.
4. Stephen F. Ackley, Dept. of the Army, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, N.H. 03755
5. Floyd Neyhart, Carrier Air Conditioning Co., Syracuse, N.Y.
6. Rexnord, Inc., P.O. Box 2022, Milwaukee, Wisc. 53201 (Mr. Anthony Geinopolos).

HIGH-GRADIENT MAGNETIC SEPARATION

Prepared by

Warren J. Lyman

I. CONCLUSIONS AND RECOMMENDATIONS

High-gradient magnetic separation (HGMS) is a new process for removing magnetic and paramagnetic particles from liquid and slurry streams. It is also possible to use HGMS for removing non-magnetic particles, but this is a complicated process requiring chemical seeding of the waste stream, and the same results can nearly always be achieved by conventional filtration and separation techniques. Therefore, in its present state of development, HGMS should be considered only when the substance to be removed is magnetic or is of sufficient value to justify investment for its recovery.

HGMS can operate at high flow rates, compared to other filtration and separation processes, and thus has potential for applications where large volume can offset costs. For example, work has been done in using HGMS to remove non-magnetic particles and dissolved metal ions from water; however, it is very unlikely that this will be commercially attractive during the next five years.

II. PROCESS DESCRIPTION

A. BACKGROUND

High-gradient magnetic separation (HGMS) is a new technique for separating weakly paramagnetic materials* and other non-magnetic suspended solids (down to colloidal particle size) from gas or liquid streams, on a large scale and at flow rates over one hundred times faster than the flow rates possible in ordinary filtration, and at lower costs and energy requirements. Magnetic separators capable of removing highly magnetic (i.e., ferromagnetic) particulates have existed for sometime; HGMS extends the capabilities of magnetic separation to include particles that are only weakly magnetic.

B. UNDERLYING PRINCIPLES

HGMS uses fine ferromagnetic filament material containing 95% void space (felted or woven steel fabric, compressed steel wool, expanded metal, etc.), and magnets capable of generating high-intensity fields [up to 20,000 gauss (G)] in large empty spaces. The impurities are collected in the filter by magnetic attraction as the feed stream passes through the unit. When the magnet is turned off, the filter matrix may be washed clean. A batch process is depicted in Figure 1; a continuous process is shown in Figure 2.

The magnetic field intensities used in conventional HGMS are in the range from 1 to 20 kG; super-conducting machines could be built to operate in the range from 20 to 100 kG. The magnetic field gradients in conventional HGMS machines are on the order of 1 kG/μm. In comparison, conventional magnetic separators have fields of about 1 kG and field gradients of about 0.1 kG/cm.

C. OPERATING CHARACTERISTICS

1. Feed Streams

HGMS is effective in removing from waste streams particles with diameters as small as one micron (.001 mm).** In comparison, conventional magnetic separators are ineffective for particles much below 100 microns in diameter. When filter matrices of steel wool are used (as is common), the wool may typically be 100 μ in diameter. Tests have indicated that this matrix is mostly effective for the removal of particles with diameters about 30 μ and that it will remove particles with diameters as low as 1 μ. At a packing density of a few percent, the average interstrand distance is on the order of 500 μ which limits the treatable particle size to about 100 μ or less. Larger particles will cause serious filter clogging problems.

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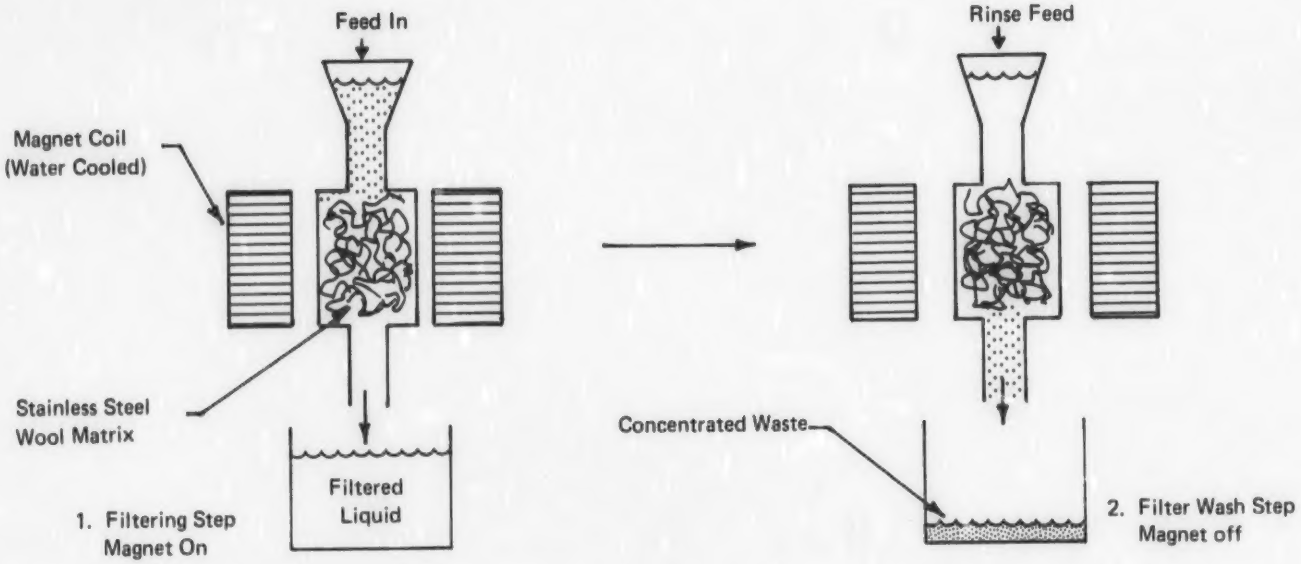
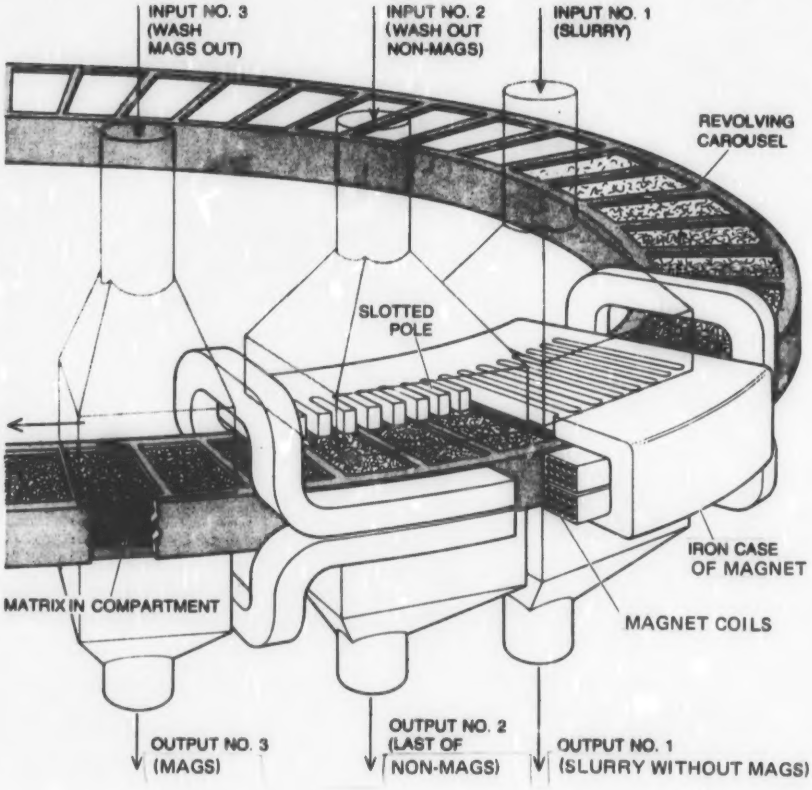
*Paramagnetic materials are those within which an applied magnetic field is slightly increased by the alignment of electron orbits. Thus the magnetic field induced in paramagnetic materials will increase monotonically as the applied magnetic field increases.

**One company has worked with particles as small as 0.1 micron.


Feed In
Magnet Coil (Water Cooled)
Stainless Steel Wool Matrix
Filtered Liquid
1. Filtering Step Magnet On
Rinse Feed
Concentrated Waste
2. Filter Wash Step Magnet off

Source: Arthur D. Little, Inc.

FIGURE 1 SCHEMATIC REPRESENTATION OF HIGH-GRADIENT MAGNETIC SEPARATION


INPUT NO. 3 (WASH MAGS OUT)
INPUT NO. 2 (WASH OUT NON-MAGS)
INPUT NO. 1 (SLURRY)
REVOLVING CAROUSEL
SLOTTED POLE
IRON CASE OF MAGNET
MATRIX IN COMPARTMENT
MAGNET COILS
OUTPUT NO. 3 (MAGS)
OUTPUT NO. 2 (LAST OF NON-MAGS)
OUTPUT NO. 1 (SLURRY WITHOUT MAGS)

Source: Ref. 1.

FIGURE 2 CONTINUOUS SEPARATION UTILIZING A ROTATING RING DIVIDED INTO COMPARTMENTS FILLED WITH MAGNETIC MATRIX

2. Process Operation

HGMS may be operated as either a cyclic or a continuous operation. Both methods are in commercial use today. Cyclic units are preferable when (1) the material being removed is a small percentage of the total volume passing through the system and/or (2) high operating pressures are needed. Continuous operation may be preferable when (1) high operating pressures are not needed and (2) the material being removed is a large percentage of the total volume passing through the system.

Under optimum conditions, HGMS can achieve very high removal efficiencies, sometimes above 95%, yielding hazardous waste concentrations in the purified stream of less than 10 ppm. In less than optimum conditions, the removal efficiencies can be quite low. Removal efficiencies will increase with (1) increasing magnetic field strength (especially for paramagnetic material), (2) increasing magnetic susceptibility of the material, (3) increasing particle size, (4) decreasing feed velocity, (5) decreasing filter matrix loading, and (6) sometimes, increasing hazardous material concentration.

3. Output Streams

The principal emission from the process is a concentrated waste stream. Particulates removed from air can be easily collected in a compact state for reuse, recycle or disposal. If matter is removed from liquid, the waste stream is a slurry with high solids content; in recent tests with steel mill effluents, the aqueous waste stream contained 30% solids (by weight). After vacuum filtration, the solids may be reused, recycled, or disposed.

A minor emission is heat, usually in the form of hot water from the magnet cooling coils. HGMS units in current use generally raise the water temperature 20-30°F. It is possible that this waste heat could be recycled for use in other processes including heating and cooling.

D. EQUIPMENT AND MATERIALS

The largest unit now in operation uses a filter canister about 84" in diameter packed with compressed magnetic stainless steel wool. The canister is surrounded by hollow conductor copper coils which energize the entire canister volume to a field of 20 kilogauss. The coils are in turn surrounded by a boxlike enclosure of steel plate which completes the magnetic circuit. These large units are rated at 400 to 500 kilowatts.

While there are no inherent design limitations on the size of HGMS units, it has been suggested that economics may limit the size range in which HGMS will find practical applications. On the large side, current HGMS units are limited (for economic and practical reasons) by the size of the components. The largest units at present can be shipped by conventional means (truck) and fairly easily installed; if they were any larger, special transportation and installation methods would be required. Thus, the power requirements of the larger HGMS units are not a crucial factor at present. For the future, superconducting magnets are seriously being considered for energy saving with very large (yet to be built) units.

III. APPLICATIONS

A. PRINCIPAL CURRENT APPLICATIONS

The principal current commercial application of HGMS in the United States is the beneficiation of kaolin (clay) to remove a small unwanted magnetic fraction. Production prototypes were tested in 1969, and the first full-scale unit was put on-stream in early 1973. Today five kaolin producers in Georgia are each operating one HGMS unit. Four of these units were supplied by Pacific Electric Motor Company (represented by Aquafine Corporation, Brunswick, GA). The fifth unit was supplied by Magnetic Corporation of America.

A wide variety of electromagnetic filter units for removing ferromagnetic particles from wet and dry materials of all kinds are sold by S.G. Frantz Company, Inc. (Trenton, New Jersey). The units generally are used to remove ferrous contaminants from product streams and employ some form of rigid grid for the filter matrix. The units are relatively small; the wet-stream filters range from about 1 to 100 gpm in capacity. These units do not employ the high magnetic fields associated with the new generation of high-gradient magnetic separators, thus they would not be considered under HGMS by most industry experts.

Electromagnetic filters – primarily for use in the power industry – are currently being sold in the United States by the Babcock & Wilcox Company (Baberton, Ohio) under license from Siemens A.G., West Germany. Information on the field strengths generated in these relatively large machines is confidential but they are probably high-gradient machines. The principal application for these machines has been the removal of magnetic suspended solids (iron compounds) from various internal water streams associated with thermal power stations; operation at high temperature and pressure is possible. One paper company in Wisconsin is using one of these machines to remove iron oxides present (at up to 32 ppm) in the steam condensate resulting from the cleaning of the paper-making machines; the purified water (still hot) is then returned to the boilers. The Babcock & Wilcox machines use a filter matrix of steel spheres ($\sim$ 40% void space) which can be loaded up to 2 to 5 g/kg of bed; it has been operated on streams with up to 100 ppm iron oxide and has been able to extract particles as small as 0.1 micron. Capacities range from about 50 gpm to over 10,000 gpm at some installations. Both feed and wash streams are upflow in these machines; washing is said to be especially rapid and complete.

The only other current commercial application is iron ore beneficiation, primarily iron ores such as hematite; units are known to be operating in Canada, Brazil and Africa.* In the United States, one unit, now out of operation, was used to process about 20 tons/hr of molybdenum ore to remove iron impurities.

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*These machines are not considered true "high-gradient" units by some industry experts. They do generate high-intensity fields but not in the large volumes that "true" HGMS units do. The high-intensity fields are present at the edges of machine-grooved plates used as the filter matrix.

Four applications are currently being investigated:

1. Beneficiation of iron ores and other ores
2. Coal desulfurization
3. Removal of flue dusts in air streams from blast furnaces
4. Water purification

Several papers have been published on the possible use of HGMS for ore beneficiation, and there is at least one pilot plant in operation, funded by the Bureau of Mines. It is estimated that HGMS ore beneficiation may have applications for over 50 different ores or metals (Ref. 2).

At least three HGMS research projects are under way in coal desulfurization. First, MIT's National Magnet Laboratory is currently looking at ash and sulfur removal from liquid coal in a project funded by the NSF and the Electric Power Research Institute. They expect to move to pilot plant trials in a year or two. Second, there is a pilot plant at Auburn University, Auburn, Alabama, and work carried out there in conjunction with Aquafine Corporation is said to have resulted in the removal of over 90% of the pyritic sulfur in liquefied coal. Third, Aquafine Corporation is investigating the potential for removal of pyrites from dry pulverized coal under a prime contract held by Indiana University. (Many other deleterious elements are also removed from coal when the pyrites are removed.)

One steel company is operating a small pilot plant to assess the potential of HGMS to remove flue dusts in air streams from blast furnaces. Ferrofluidics Corp. (Burlington, MA) is working on an application for the removal of particulates from smoke stacks. An atomized flerrofluid is introduced into the stack and it apparently collects the particulates; the ferrofluid is then collected magnetically.

One magnetic separator unit was installed in Freehold, New Jersey, as part of a waste water treatment system (Ref. 3). Because the magnetic separator was part of a whole waste treatment system, it was difficult to assess the efficiency and costs of the magnetic unit alone. The magnetic separator was used for about one year and then removed, primarily because they found it was not needed; the clarifier was reducing suspended solids to a low enough level so that the clarifier effluent could be sent directly to the carbon column. It was noted, however, that the efficiency of the magnetic separator was low ($\sim$ 50-60%) when the concentration of suspended solids in the feed was low; they had expected removals of 80% or more. Apparently removal efficiencies of 90-95% were obtained when the concentration of suspended solids in the feed was high.

In 1973, the Massachusetts Metropolitan District Commission (MDC) evaluated a solicited proposal for the use of an HGMS unit to clean up the Charles River (Ref. 4). The MDC was impressed by the capabilities of the proposed HGMS plant, but did not contract for the work because, at the time (late 1973), the costs seemed to outweigh the benefits.

No other waste water treatment units are in use. Water purification applications are currently being explored by Sala Magnetics, Inc., of Cambridge, Massachusetts and at MIT's National Magnet Laboratory.

When HGMS is used to purify waters containing non-magnetic colloidal material, the feed solution is seeded with magnetite (Fe_3O_4), up to 1000 ppm, and then treated with a flocculating electrolyte (e.g., aluminum sulfate). The non-magnetic contaminants associate themselves with the resulting magnetic floc and can thus be filtered out by HGMS. Flow rates of 50-150 gal/min/ft^2 have been achieved in laboratory operations.

An example of the removal of non-magnetic suspended solids is given in Table 1.

TABLE 1

HGMS REMOVAL OF NON-MAGNETIC SUSPENDED SOLIDS FROM WATER

Treatment Steps:

1. Addition of approximately 1000 ppm iron oxide seeding material;
2. Addition of aluminum sulfate (1-2 ppm Al^{+3}) as flocculating electrolyte; and
3. Treat with high-gradient magnetic separation.

	Charles River Sample				Deer Island Sewage Sample	
	Surface		Bottom			
	Control	Treated	Control	Treated	Control	Treated
Coliform Bacteria (/100ml)	16,000	0	16,000	300	2.8×10^6	18,000
Turbidity JTU units	20	2	1,700	1	50	3
Color (color units)	105	3	3,700	1	150	20
Suspended Solids (mg/liter)	7	5	690	5	45	9

Source: Ref. 5

B. POTENTIAL APPLICATIONS TO WASTE TREATMENT

Generally, HGMS can be used if: (1) the wastes can be made to flow through a relatively open filamentary matrix (95% void space), (2) the wastes are finely divided, and (3) the feed stream is not too corrosive to iron or steel. Potentially treatable waste forms are: (1) liquids (aqueous and non-aqueous), (2) slurries, and (3) dry powders. Not treatable are sludges, tars, and gases.

Removable compounds fall into three groups: (1) paramagnetic (or ferromagnetic) elements and compounds, (2) non-magnetic suspended solids, and (3) dissolved material in water. Each group is described below:

(1) Paramagnetic Elements and Compounds (as suspended solids) are all removable by HGMS. Even very weakly paramagnetic materials may be removed. Considering the first 104 elements, the breakdown is as follows (Ref. 1):

	Elements	**Compounds**
a.	3 are ferromagnetic (Fe, Co, Ni)	Either ferromagnetic or paramagnetic
b.	55 are paramagnetic (except N and Cu, which are slightly diamagnetic in pure form)	32 form paramagnetic compounds (Sc, Ti, V, Cr, Mn, Y, Mo, Tc, Ru, Rh, Pd, Ta, W, Re, Os, Ir, Pt, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, U, Pu, Am) 16 form diamagnetic compounds (Li, O, Na, Mg, Al, Ca, Ga, Sr, Zr, Nb, Sn, Ba, La, Hf, Lu, Th) 7 elements become paramagnetic when one or more are present in a compound (N, K, Cu, Rb, Cs, Au, Ti)
c.	Of the remaining 46 elements, all but 16 have diamagnetic properties	

(2) Non-Magnetic Suspended Solids may be removed from a contaminated stream if they associate with a magnetic floc [e.g., $Fe_3 O_4 + Al_2 (SO_4)_3$] which can be added to the stream (Refs. 1, 5, 6). Tests have been carried out (Ref. 5) to show that HGMS can remove suspended solids, color bodies, other particulates associated with turbidity, *and bacteria* from polluted water.

(3) Dissolved Material in Water may be removed by HGMS if it coprecipitates with a ferric hydroxide gel in the waste stream (Ref. 7). The following ions may be coprecipitated for removal:

Be^{2+}, B^{3+}, Al^{3+}, Si^{4+}, $P(PO_4{}^{3-})$,

3^{rd} transition metal ions, Zn^{2+}, Ga^{3+},

Ge^{4+}, $As^{3+,5+}$, Y^{3+} and rare earth metal

ions, Zr^{4+}, Nb^{n+}, Cd^{2+}, In^{3+},

Sn^{4+}, Ba^{2+}, Pb^{2+}, Bi^{3+}, U^{n+}.

HGMS is probably best suited for the removal of magnetic hazardous wastes that are present in low concentrations in a liquid waste stream. Removal of non-magnetic material may be effected by seeding with a magnetic material plus a flocculant, but this is not likely to be cost competitive with processes such as froth flotation and centrifugation.

The maximum concentration of removed hazardous material that can be attained in the filter backwash may be on the order of 10% *by volume* when a steel wool filter matrix is used*; large variations from this number are possible and will depend primarily on the magnetic strength (or susceptibility) of the material removed and the efficiency of backwashing. In order to achieve relatively high concentration factors with HGMS, the feed concentration should probably be at least an order of magnitude lower than the backwash concentration.

Current work in clay and ore beneficiation has shown that slurries with up to 10 or 15% solids (by volume) can be passed through matrices such as steel wool. HGMS would be applicable for the treatment of such a stream if the hazardous wastes (1) were only a small fraction of the total solids, and (2) were ferromagnetic or paramagnetic.

One area of specific activity is the treatment of aqueous wastes from steel mills (Ref. 8); pilot studies have been done, and a new pilot plant with a capacity of 500 gal/min is currently in operation. No government funding is involved in this project. The company expects that the first commercial sale of an HGMS unit for wastewater treatment could come as soon as two years from now. An example of the scale of treatment involved is the treatment of a feed stream with 50 ppm solids; removal efficiencies are 90-95%, and the concentrated waste stream comes out with 30% solids.

The Canadian Atomic Energy Commission has carried out pilot studies to assess the potential of HGMS for the removal of contaminants (e.g., corrosion products, radioactive particles) in the D_2O loop of a nuclear reactor. Some companies are also looking in general at the applicability for boiler water treatment. It is expected that the general area of trace metal removal (from water) is a good application area for HGMS.

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*This is based on a factor of two times the volume of the filter matrix, which will be around 5% in a typical application.

An EPA study on the applicability of HGMS to the treatment of combined sewer overflow is currently being carried out at Sala Magnetics, Inc. Preliminary results are said to be encouraging; removals for some pollutants are equivalent to secondary or tertiary treatment, and the indicated costs are reasonable. The combination of high flux rate and small unit space requirements makes HGMS an attractive possibility for the treatment of combined sewer overflow.

IV. ENERGY, ECONOMICS, AND ENVIRONMENTAL ISSUES

A. ENERGY REQUIREMENTS

Table 2 lists the energy requirements (magnet power ratings) for various sized units. All units are of the cyclic type which employ the use of a cylindrical filter canister.

New magnet designs are said (Ref. 1) to require only a tenth of the power required by conventional separators. While no data was available to ADL on the actual electrical energy requirements, the magnitude involved must be considered large. As was mentioned above, the largest clay beneficiation units being used today are rated at 400 kW.

TABLE 2

ESTIMATED CAPITAL COSTS FOR HGMS UNITS

Type of Use	Volume Treated (gpm)	Canister Diameter (in.)	Magnetic Field Generated (kG)	Unit Power Rating (kW)	Approximate Capital Cost ($)*
Ore Beneficiation	1,000	84	20	400	800,000
	1,000	84	10	200	400,000
	240	42	20	100	130,000
	240	42	10	50	70,000
	6	4	20	100	40,000
Removal of Highly Magnetic Material	30	8	1-2	20	5,000
Municipal Water Treatment**	30,000	–	1-2**	?	2,000,000

*Includes magnet, canister, filter, power supply, automatic controls, and magnet cooling system.

**Several units required; relatively low magnetic fields are required since water is seeded with a highly magnetic material.

Source: Arthur D. Little, Inc., estimates.

B. ENVIRONMENTAL ISSUES

There are no serious environmental issues associated with the use of HGMS. It is expected that the most likely future waste treatment applications of HGMS will be for material recovery from water or slurries. If material recovery was not included at a HGMS installation, then the sludge from the filter backwash would have to be disposed of. The relatively large electrical energy requirements are a possible environmental concern, but this too may be considered a minor issue if material recovery is being effected.

C. ECONOMIC ANALYSIS

The costs of treatment with HGMS depend on several factors – field strength needed, volume to be treated, solids content – and the only current commercial application in the United States, clay beneficiation, may not be considered typical of hazardous wastes. Preliminary cost estimates for water treatment indicate that HGMS is competitive with conventional treatment systems (Ref. 1). The space requirements (an important consideration in many urban areas) are substantially smaller.

Capital equipment cost and estimates based on some current industry quotes are given in Table 2. Operating costs for HGMS are in the range of $1/1000 gal for clay beneficiation. Operating costs for municipal wastewater treatment have been estimated to be as low as 5¢/1000 gal for a 50 MGD plant; another estimate put the costs at 10-15¢/1000 gal for a 40 MGD plant; a third estimate put the costs at 50¢, 21¢, and 15¢ per 1000 gal for a 1 MGD, 10 MGD and 100 MGD plant, respectively. Operating costs for the treatment of steel industry wastewaters have been estimated at 6¢/1000 gal; in this case the "hazardous materials," being mostly iron compounds, have relatively high magnetic susceptibilities and thus do not require very high magnetic gradients for removal.

It seems reasonable to conclude that operating costs for the removal of weakly magnetic material will be of the order of $1-5/1000 gal. Removal of highly magnetic material may involve much lower costs, perhaps of the order of 10-50¢/1000 gal.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

High gradient magnetic separation (HGMS) is most appropriate for removing magnetic and paramagnetic particles from liquid and slurry streams. When non-magnetic particulates are present, the magnetic material should constitute only a small fraction of the total solids; total solids, however, may be as high as 10-15% by volume of the waste stream. The process will probably not be competitive economically for low volume waste streams, e.g., for streams below about 50 gpm.

It is also possible to use HGMS for removing non-magnetic particles, but this is a more involved process requiring chemical seeding of the waste stream, and the same results can nearly always be achieved by conventional filtration and separation techniques. When the target material is non-magnetic, HGMS must compete with the following processes capable of dealing with fine matter:

- Gravity separation
- Inertial separation
- Electrostatic precipitation
- Froth flotation, and
- Filtration

Most of these processes are very inexpensive and very widely used. HGMS can handle larger volumes, and it extends the lower limit of particle size collection significantly, and thus it has the potential to compete with these processes. However, in its present state of development, HGMS should be considered only (1) when the substance to be removed is magnetic or is of sufficient value to justify investment for its recovery, or (2) when space restrictions require the use of a process allowing high treatment rates in a small space.

Because HGMS can operate at high flow rates, compared to other filtration and separation processes, it has potential for applications where large volume can offset costs. For example, work has been done in using HGMS to remove non-magnetic particles and dissolved metal ions from water. One company expects that the first commercial sale of an HGMS unit for water pollution control could come in about two years; however, other experts in the field estimate that it will be 5 to 10 years before HGMS could be widely applied to water pollution problems. (A similar or longer time frame may be necessary for the development of units to remove particulates from gaseous streams.) This time frame could be shortened as a result of the relatively active work currently going on in ore beneficiation and coal desulfurization via HGMS. Many of the magnet and process improvements developed there would be transferable to units for treating hazardous waste streams.

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A. REFERENCES

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B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD

The following individuals and companies were contacted by ADL for information on HGMS. The contacts given below in listings 1-5, and 10 may be considered experts in the field of HGMS. Additionally, research and development (or other investigations) of this process is currently being carried out by at least eight other universities, seven industrial groups, and two government groups. The names of these individuals may be obtained from ADL upon request; many can be identified in the list of references that follows below.

1. Dr. Robert Kaiser (Winchester, Mass.); expert in magnetic separation methods.

2. Sala Magnetics, Inc. (Cambridge, Mass.): company manufactures high-gradient magnetic separators.

3. Dr. J. Iannicelli, Aquafine Corp. (Brunswick, Georgia): company represents Pacific Electric Motor Co. (manufacturer of high-gradient magnetic separators).

4. Dr. Z. J. J. Stekly, Magnetic Corporation of America (Waltham, Mass.): company manufactures high-gradient magnetic separators.

5. Drs. Henry Kolm and David Kelland, Massachusetts Institute of Technology, Francis Bitter National Magnet Laboratory (Cambridge, Mass.): conducting research in HGMS.

6. Charles Pugh and Mr. Brinkman, Stearns-Rodger (Denver, Colo.): former distributors of Jones HGMS units.

7. Gerald Curtis, Magnetics International (Montreal, Quebec): distributor of Jones HGMS units.

8. Walter Reed, Ferrofluidics Corp. (Burlington, Mass.): company manufactures ferrofluidic devices.

9. S. G. Frantz Co. (Trenton, N.J.): company manufactures magnetic separators.

10. Dr. Y. A. Liu, Professor of Chemical Engineering, Auburn University (Auburn, Ala.): working on coal desulfurization via HGMS; general chairman of conference on magnetic desulfurization of coal at Auburn U., March 23-25, 1976.

11. Martin Cosgrove, Massachusetts Metropolitan District Commission (Boston, Mass.): evaluated a solicited proposal to clean up the Charles River basin via HGMS.

12. Wallace Johnson, Hercules, Inc. (Wilmington, Del.): company designed and operated (temporarily) the waste treatment plant in Freehold, N.J. that incorporated a magnetic separator.

13. Dr. Erwin Kugelman, U.S. EPA (Cincinnati, Ohio): contract monitor on Freehold project (see item above).

HYDROLYSIS

Prepared by

Lawrence N. Davidson

I. CONCLUSIONS AND RECOMMENDATIONS

Hydrolysis is widely applicable to organic wastes. In addition it has the potential for treating more types of waste streams than those for which it is currently being used.

Toxic products or by-products can be a problem, however. We recommend this process for consideration as a waste treatment.

II. PROCESS DESCRIPTION

A. BACKGROUND

Hydrolysis as a chemical process has been used since the earliest days of soapmaking. The addition of alkali to hydrolyze heated fats in the production of soap is still practiced today. Processes involving hydrolysis are common in industry, although frequently they are called by different names. (Example, the hydrolysis of fats mentioned above is termed saponification.) Hydrolytic processes have commercial manufacturing applications in such diverse industries as food, paper, and petrochemicals.

B. UNDERLYING PRINCIPLES

The term hydrolysis applies generally to reactions in which water brings about a double decomposition, with hydrogen going to one component and hydroxyl to the other (Refs. 1,2). The general formula is $XY + H_2O \rightarrow HY + XOH$; examples from organic and inorganic chemistry are respectively

$$C_5H_{11}C\ell + H_2O \rightarrow HC\ell + C_5H_{11}OH \text{ and}$$

$$KCN + H_2O \rightarrow HCN + KOH$$

Hydrolysis is a specific type of solvolysis, alcoholysis and ammonolysis being other common cases. The distinction between hydrolysis and hydration is not clear and is defined mostly by common usage. The reaction $K_2O + H_2O \rightarrow 2KOH$ is hydration, while the saponification of a nitrile $C_2H_5CN + H_2O \rightarrow C_2H_5CONH_2$ is hydrolysis. In general it is necessary for a bond between two atoms to be broken in hydrolysis, but the term is sometimes used for reactions in which one bond of a multiple bond is broken as in the nitrile example.

Inorganic hydrolytic reactions in which a salt reacts with water to form acid and base are usually the reverse of neutralization. The trivalent metal salts of aluminum and iron undergo a different mechanism of hydrolysis; during a series of reactions with water, various multivalent hydrous oxides (Ref. 3) are formed. These charged species are important in floc formation, and the treatment, by coagulation, of turbid waters.

Organic hydrolysis may take on a broader aspect and include reactions in which water is not a reactant. For example, the addition of an alkali to solution and the subsequent formation of the alkali salt of an organic acid is described as hydrolysis. Although water by itself can bring about hydrolysis, most commercial processes employ elevated temperatures and pressures to promote reaction. Acids, alkalies, and enzymes are commonly used as catalysts although an alkali can also frequently participate as a stoichiometric reactant. Hydrolytic reactions may be broken down into five classes (Ref. 2).

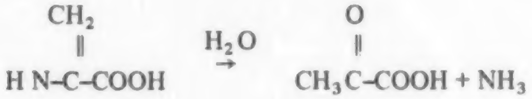
1) Pure hydrolysis with water alone,
example: $C_6H_5SO_3H + H_2O$ (steam) $\rightarrow C_6H_6 + H_2SO_4$;

2) Hydrolysis with aqueous acid, dilute or concentrated,
example: $CH_3COOC_2H_5 + H_2O \xrightarrow{HC\ell} CH_3COOH + C_2H_5OH$;

3) Hydrolysis with aqueous alkali, dilute or concentrated,
example: $C_6H_5C\ell + NaOH (aq.) \rightarrow C_6H_5OH + NaC\ell + H_2O$;

4) Alkali fusion, with little or no free water, but at high temperatures – the reaction is the same as class 3, with a decreased water ratio;
example: $C_6H_5SO_3Na + 2NaOH \rightarrow C_6H_5ONa + Na_2SO_3 + H_2O$; and

5) Hydrolysis with enzymes as catalysts. For example, in the biological degradation of carbohydrates, fats, and proteins, hydrolysis by enzymes is often the first step to degrade these compounds to a size which can pass the cell membrane of bacteria (Ref. 4) e.g.,



$$HN{-}\overset{\overset{\displaystyle CH_2}{\|}}{C}{-}COOH \xrightarrow{H_2O} CH_3\overset{\overset{\displaystyle O}{\|}}{C}{-}COOH + NH_3$$

The agents for acid hydrolysis most commonly used are hydrochloric and sulfuric acids, but many others are of potential use (formic, oxalic, benzenesulfonic, etc.). Alkaline hydrolysis utilizes sodium hydroxide most frequently, but the alkali carbonates as well as appropriate potassium, calcium, magnesium, and ammonium compounds could find applications.

In conclusion, hydrolysis may be used for synthesis or decomposition of a chemical compound. An example of a change in which hydrolysis is used for synthesis is the reaction between water and ethyl cyanide: $C_2H_5CN + 2H_2O \rightarrow C_2H_5COONH$. Decomposition may be illustrated by the hydrolysis of a diazonium salt: $C_6H_5\underset{\substack{| \\ C\ell}}{N} \equiv N + H_2O \rightarrow C_6H_5OH + N_2 + HC\ell$.

C. OPERATING CHARACTERISTICS

1. Feed Streams

Treatment by hydrolysis is applicable to wastes with a variety of physical forms. Feed streams can be either liquids or gases, aqueous or non-aqueous solutions, slurries, sludges, or tars. Both organic and inorganic chemicals can be hydrolyzed. The applicability to organic chemicals includes aliphatics and aromatics, esters, ethers, carbohydrates, sulfonic acids, halogenated compounds, amides, phosphates, and nitriles (Ref. 1).

2. Process Operation

Because of the variety of waste streams amenable to hydrolysis, a wide range of treatment schemes has to be considered – batch vs. continuous, tank vs. tower, etc.

The hydrolyzing reagent may be of any physical form – solid, liquid, or gaseous. In actual practice, the treatment chemical is usually a mineral acid (such as sulfuric or hydrochloric) or an alkaline solution (such as sodium or potassium hydroxide). Upon occasion the reagent may be added as a slurry or even as a dry solid, as in the case of lime. For certain reaction schemes the use of metal or enzyme catalysts can be considered (Ref. 5). For acid or alkaline hydrolysis the rate is proportional to the concentration of promoter, particularly in dilute solutions. Concentration is particularly important in cases where side reactions may occur.

The operating conditions for hydrolysis have to be selected to optimize the specific reaction desired. Many hydrolytic processes proceed at accelerated rates at elevated temperature (the speed of hydrolysis doubles approximately for every 10° rise in temperature). Hydrolytic reactions follow the common rules of kinetics and thermodynamics, with respect to rates and equilibria. Upon occasion, high reaction rates and conversions may be incompatible. An example would be a hydrolysis which proceeds slowly at moderate temperatures, but yields an undesirable product at higher temperatures (due to an equilibrium shift). A catalyst would be an appropriate solution to this problem.

3. Output Streams

Depending on the particular reaction, treatment products may be in the liquid, gaseous, or solid state. In particular, high temperature hydrolysis may produce vapor products. Solid products may be in the form of slurries, sludges, or even tars. In certain hydrolytic reactions, more than one product phase may be formed. Each phase may have a density different from the original material, and a separation may be effected. An example is the hydrolysis of the low density solid, polyurethane, which hydrolyzes to toluene diamine and polyol phases; also, the total volume is reduced by a factor of about 30 (Ref. 8).

The treated stream may possibly contain components as hazardous or more hazardous than the original waste. A toxic pesticide, parathion, is a good example. Although it is an unusually stable organophosphate, under the proper conditions it can undergo hydrolysis. One of the hydrolytic products is p-nitrophenol, which is quite toxic. Also, the use of acid or alkali to promote hydrolysis may necessitate pH adjustment of the treated waste stream before discharge.

D. EQUIPMENT AND MATERIALS

1. Equipment

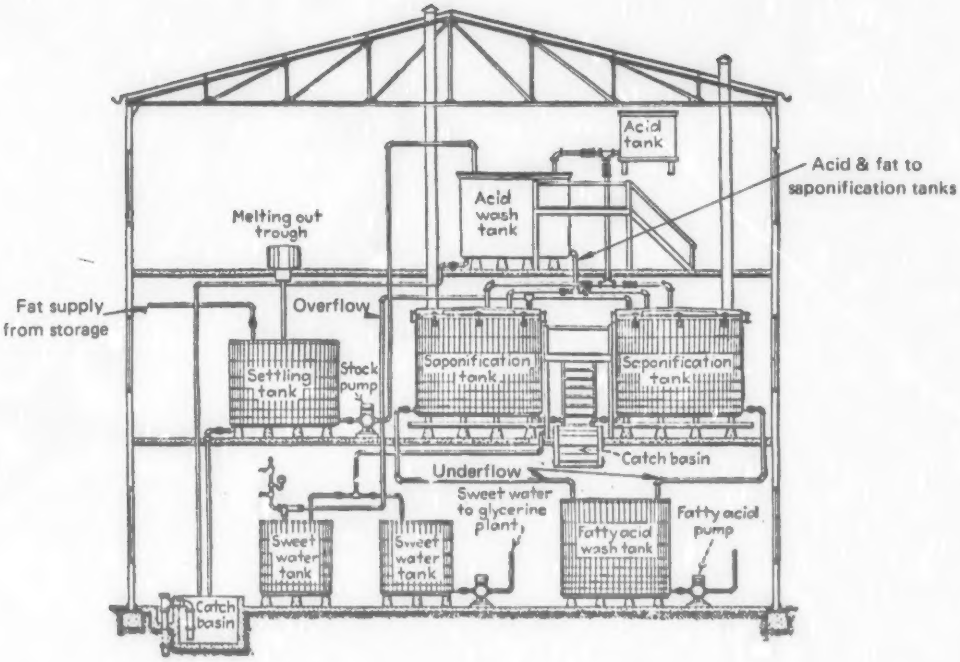
Industrial applications utilize a wide variety of equipment to carry out hydrolysis reactions, such as countercurrent towers, tubular reactors, tray-type contactors, autoclaves, open tanks, and pressure vessels. The design for each reactor depends on the phase of the reactants and the reaction rate (as a function of temperature and pressure). Ancillary equipment might include storage facilities, pumps, agitators, heaters, compressors, and settlers – dependent on the specific reaction. Often, due to the acidic/basic nature of hydrolysis, a neutralization scheme is necessary.

The selection of continuous vs. batch equipment is both an economic and a design decision. In general, batch equipment, e.g., tanks, is less expensive and easier to operate, but subject to size limitations. Handling large volumes of material requires large tanks which not only become expensive but also may involve physical space problems. Continuous operation is suited for large flow rates and relatively short residence times. It may be carried out in backmix flow (using a stirred tank or series of tanks), or in plug flow (as in the tubular autoclave), both of which are cases of ideal reactors. Other reaction schemes with towers (cocurrent or countercurrent) usually involve mass transfer as well as kinetic considerations. The elevated pressures often present in hydrolysis can also limit the choice of equipment. Pressures above about 1000 psi frequently require the use of an autoclave, either batch or continuous.

To provide some insight into actual equipment for specific applications, several examples will be presented, related to the hydrolysis of fats and oils:

- The Twitchell process (Ref. 2) – This is the traditional method for producing fatty acids in a batch. The basis of the process is heating the fat with live steam for 24 hours in the presence of a hydrolyzing reagent, and subsequent separation of products. The system consists of a settling tank, several saponification tanks, wash tanks, storage tanks, and a variety of pumps (gravity flow is used wherever possible) as shown in Figure 1.

- Countercurrent hydrolysis of fats (Ref. 7) – This is the more modern method for manufacturing fatty acids and glycerol in a continuous flow system. The fatty oil feed is contacted with water in a countercurrent tower, under steam pressure. Fatty acids are discharged from the top, while aqueous glycerine comes out the bottom. The time required to produce fatty acids in continuous flow is hours instead of the days necessary for batch operation. The equipment includes deaerators, a hydrolysis tower, a decanter, storage tanks, and several pumps. The hydrolysis tower is on the order of 2-3 feet in diameter and 70-80 feet high, capable of operating at about 240-260°C 700-750 psi. A tower with these specifications can hydrolyze about 10,000 lb/h of fatty oil (with about 6,000 lb/h of water).


Acid tank
Acid & fat to saponification tanks
Acid wash tank
Melting out trough
Fat supply from storage
Overflow
Settling tank
Stock pump
Saponification tank
Saponification tank
Catch basin
Underflow
Sweet water to glycerine plant
Fatty acid pump
Sweet water tank
Sweet water tank
Fatty acid wash tank
Catch basin

Source: Ref. 2.

FIGURE 1 THE TWITCHELL PROCESS

- Hydrolysis of fatty acid discharge in a flue gas – Figure 2 (Ref. 6) illustrates the use of hydrolysis in a waste treatment system. The fat droplets are scrubbed in a venturi and separated in a fat trap. Calcium hydroxide is added to the fatty acid and the mixture under pressure is sent to a settling tank. Upon letdown of the pressure, heavy metal soaps are bubbled to the surface and skimmed off. The actual equipment used in the hydrolysis consists of the fat trap, a retention tank, a settling tank, storage tanks, and pumps.

These three examples represent the same industrial process, i.e., hydrolysis of fats, yet the equipment is different in each case. The first process is a simple batch performed in tanks; the second is continuous flow in a tower; and the third is continuous flow in tanks. The hydrolysis tower can be of different designs, since some operations require trays in the column while others need only a hollow pipe.

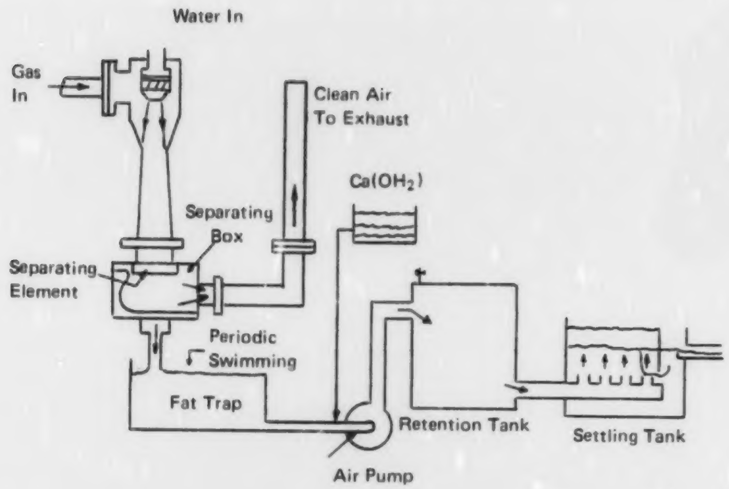
As an example of a type of non-standard equipment which may be employed, the Dow process for making phenol from chlorobenzene uses a tubular autoclave in the hydrolysis step (Refs. 1,2). The autoclave is 4,500 linear feet of 1-1/2 inch Schedule 160 steel pipe, and the interior conditions reach about 4,000 psi at 370°C. Flow through such a reactor is on the order of 8,000 lb/h. Schedule 160 pipe (wall thickness of 0.28 in.) is required based on the design-allowable stress at the described operating temperature and pressure.

2. Materials

Commercially most hydrolytic processes occur under acidic or basic conditions, which are corrosive. Care must be exercised in selecting materials of construction to provide reasonable service-life for equipment. There are several types of corrosion, but for present purposes, it need only be stated that chemical attack by acid or alkali shortens the useful life of equipment. Examples of materials recommended for handling different acids and alkalies at ambient temperatures are (Ref. 6):

Sulfuric acid (75-95%) – lead
    (< 10%) – lead or rubber
Hydrochloric acid (conc. or dilute) – rubber
Sodium hydroxide (conc.) – 316SS or rubber
    (dilute) – 316SS, rubber, carbon steel, or cast iron.

At higher temperatures the corrosivity of most chemicals increases, and allowances must be made for greater materials deterioration. Other chemically resistant materials include: glass, wood, metal alloys such as monel, and plastics, e.g., PVC. Lead, rubber, glass, and plastic are often used as liners in corrosive processes.


Water In
Gas In
Clean Air To Exhaust
Ca(OH2)
Separating Box
Separating Element
Periodic Swimming
Fat Trap
Retention Tank
Settling Tank
Air Pump

Source: Ref. 6.

FIGURE 2 HYDROLYSIS OF FATS

III. APPLICATIONS TO DATE

A. PRINCIPAL CURRENT APPLICATIONS

Hydrolysis has been employed for many years, and finds extensive use in the manufacture of organic materials. Some general examples of applications are:

- Hydrolysis of ethers – ethylene oxide from ethylene glycol.
- Hydrolysis of carbohydrates – conversion of wood cellulose to edible sugars, and decomposition of starch to dextrose.
- Hydrolysis of aromatic sulfonic acids – phenol from sodium benzene sulfonate by alkali fusion.
- Hydrolysis of aliphatic halides – amyl alcohols from chloropentanes.
- Hydrolysis of amyl or allyl chlorides – production of alcohols.
- Hydrolysis of ethylene chlorohydrin – production of ethylene oxide and ethylene glycol.

To more completely illustrate hydrolytic processes, several examples will be discussed in more detail.

- Hydrolysis of an aromatic halide, production of phenol from chlorobenzene (Ref. 1) – The Dow process hydrolyzes chlorobenzene in continuous flow with caustic soda, and has a phenol yield about 85% of theoretical. The charge of chlorobenzene, diphenyl ether (to prevent a side reaction), and aqueous caustic soda (10% by weight) reacts in a tubular autoclave, about 4500 ft in length, at about 370°C and 4,000 psi.
- Production of fatty acids from fatty oils (Ref. 7) – Triglycerides, e.g., tallow, are hydrolyzed to fatty acids in the absence of acid or alkali as indicated by the sample reaction:

  $$(C_{17}H_{35}COO)_3C_3H_5 + 3H_2O \rightarrow 3C_{17}H_{35}COOH + C_3H_5(OH)_3$$

  In countercurrent towers, water contacts the oil at 700-750 psi and 240-260°C under high pressure steam; glycerol and fatty acids are produced and separated. About 98% of the glycerides can be hydrolyzed, with residence times on the order of an hour or more. In some operations metal oxide or hydroxide catalysts are used.

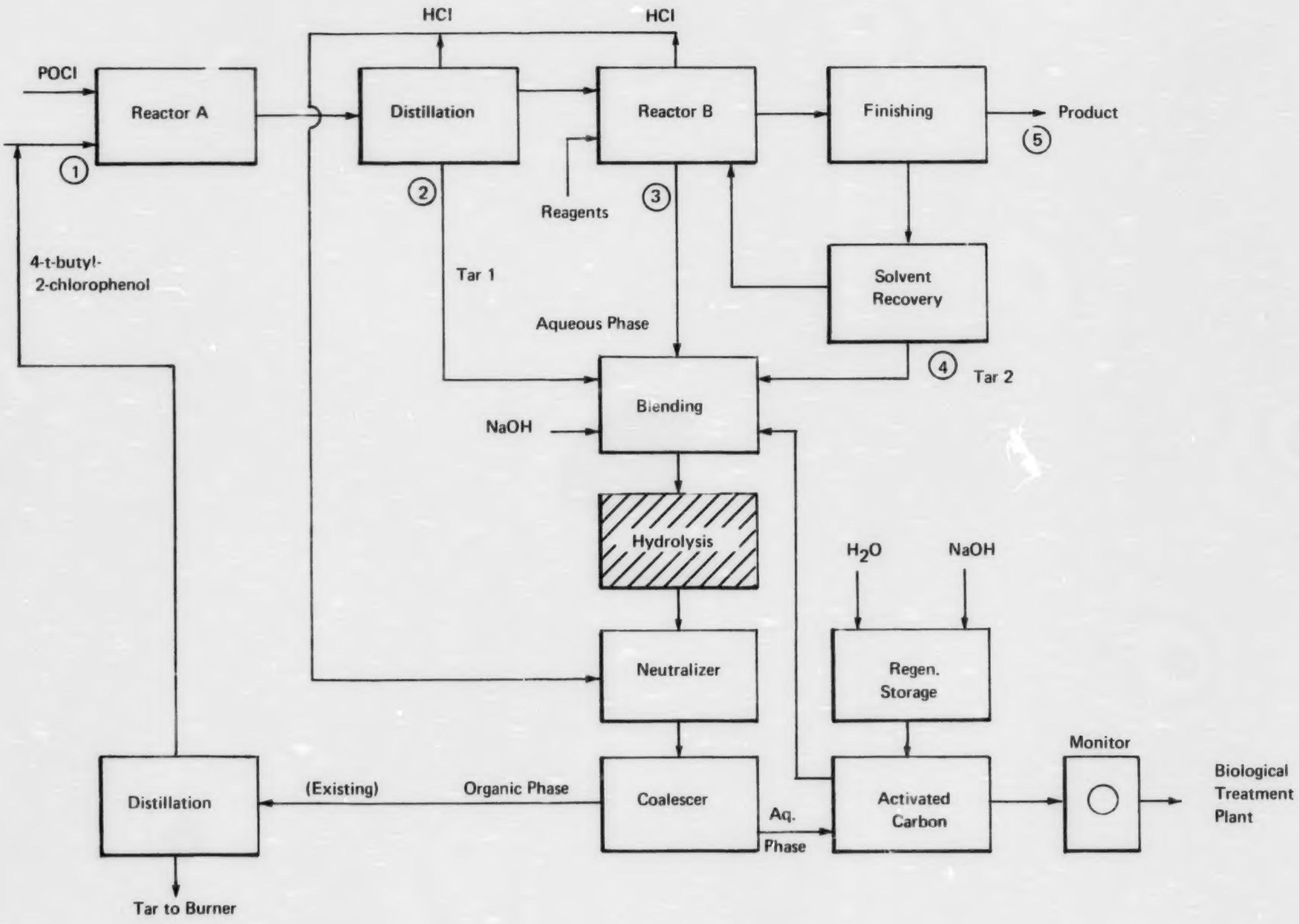
- Manufacture of titanium dioxide – This is an example of the application of hydrolysis to inorganic processes. A concentrated solution of titanium sulfate contacts hot water and is boiled in a tank of about 20,000 gal. The temperature is maintained at 115°C by steam injection for three hours, after which the titanium dioxide is recovered by filtration. The reaction could also be carried out under pressure at a reduced temperature.

The principles and equipment used in waste treatment are the same as in manufacturing applications. Hydrolysis is presently not widely employed as a treatment for industrial wastes. Equipment and operating costs frequently may turn out to be prohibitive. Several different treatment techniques are demonstrated in the following examples:

- Treatment of acid sludge (Ref. 9) – In the petroleum industry sludge from the acid treatment of light oils is often hydrolyzed. 50 percent or more of a refinery's acid requirements can be obtained from acid sludge. Upon water hydrolysis, sulfuric acid sludge forms two phases; a weak sulfuric acid layer, and a tarry acid oil layer. The former is recovered by concentration, and the latter is burned as fuel.

- Recycle of waste stream in an organic chemicals plant (Ref. 10) – Dow Chemical, until recently, operated a hydrolytic treatment process in the manufacture of crufomate, an aromatic phosphoramidate, a starting material for an insecticide. A process flow sheet is shown in Figure 3. The process generates 15 pounds of wastewater per pound of product, and also two tar streams (0.65 lb/lb product). Most of the hydrolysis of the three streams occurs in a high temperature hydrolysis coil (240°C, 10 minutes residence) with several wt % caustic soda. The overall hydrolysis is greater than 98% and produces two streams; an aqueous phase slated for biological treatment and an organic phase, which is distilled and recycled. A process flow sheet is shown in Figure 3. The process was quite effective but was shut down due to an oversupply of the product.

- Degradation of pesticides – Many pesticides are subject to deterioration in acid or most often alkaline media. Carbamates and organophosphorus compounds can be hydrolyzed under the correct temperature and pH conditions. One organophosphate plant uses an enclosed glass-lined reaction vessel to hydrolyze waste. One part of 20% caustic solution and 30 parts of waste are hydrolyzed in a batch at 93°C for 1.5 hours (Ref. 11). Another manufacturer suggests the use of an aqueous caustic soda and detergent solution to decontaminate containers and dispose of pesticide (Ref. 12). Subsequent burial of the container and rinse solution are recommended. The production of unidentified species, or species of unknown toxicity is a problem in the hydrolysis of pesticides and requires careful study in any treatment scheme.


POCl
Reactor A
①
4-t-butyl-
2-chlorophenol
HCl
Distillation
②
Tar 1
HCl
Reactor B
Reagents
③
Aqueous Phase
Finishing
Product
⑤
Solvent
Recovery
④
Tar 2
Blending
NaOH
Hydrolysis
H_2O
NaOH
Neutralizer
Regen.
Storage
Monitor
Distillation
(Existing)
Organic Phase
Coalescer
Aq.
Phase
Activated
Carbon
Biological
Treatment
Plant
Tar to Burner

Source: Ref. 10.

FIGURE 3 THE CRUFOMATE PROCESS

- Removal of fats from exhaust flue gas – The system illustrated in Figure 2 shows the scrubbing of fatty acid droplets from the gas and the following hydrolysis with lime. This case embodies the direct use of a manufacturing process, saponification, for waste treatment.

B. POTENTIAL APPLICATIONS TO WASTE TREATMENT

There are several processes employing hydrolysis which show promise for the future treatment of industrial wastes.

- Conversion of sludge to animal feed (Ref. 13) – This process converts activated organic sludge to a thick syrup, high in protein, carbohydrates, and vitamins. The hydrolysis step consists of heating in the presence of water and sulfur dioxide. Filtration efficiency is greatly improved and the moisture content of the filter cake is reduced.

- Hydrolysis of polyurethane foam (Ref. 8) – Ford Motor has worked for several years developing a process to decompose polyurethanes. A small pilot unit is being constructed using a tubular reactor which will operate at about 250°C. Steam will be utilized to hydrolyze the plastic, allowing operation at atmospheric pressure. The hydrolysate occurs in two liquid phases; the upper phase is an aqueous solution of toluene diamines, and the lower is a polyol. The diamines can be converted into toluene diisocyanate and used with the polyol to produce polyurethane again. General Motors is involved in a similar project employing hydrolysis of polyurethane with steam at atmospheric pressure and about 315°C (Ref. 14). Although polyurethane itself is not a hazardous waste, a similar processing scheme involving hydrolysis can undoubtedly be used on other organic and polymeric wastes.

- Acid hydrolysis of cellulose (Refs. 15,16) – Development of a method for hydrolyzing paper refuse is currently under way at Dartmouth College. Small-scale batch experiments have been completed and a plug flow reactor is now under study. The hydrolysis entails addition of concentrated sulfuric acid to a slurry (about 15% solids); the acid concentration after mixing should be about 1%. At 232°C (400-500 psi) and a residence time on the order of one minute, the conversion of cellulose should be about 50%. The actual reaction involves the decomposition of cellulose in the refuse to glucose, catalyzed by the acid. The product sugar could be fermented to ethanol (enzymatic hydrolysis) or converted to other materials, e.g., amino acids. The more concentrated the paper slurry, the less acid required, since sulfuric acid behaves as a catalyst – also, the more glucose produced. However, practical problems arise in handling concentrated slurries, such as pumping and heat transfer. Although the process has been tested only on paper refuse, it is readily applicable to treating paper mill wastes, e.g., from sulfite or kraft pulping, and other organic matter with structures similar to cellulose (carbohydrates).

Waste streams containing carbohydrates may be found in the effluents from dairies, wool-scouring operations, and antibiotics manufacture. These wastes can be hydrolyzed by enzymes or acid; alkalies are not usually useful for carbohydrates. Hydrolysis of streams containing fats and oils (esters) from the food industries and petroleum/petrochemical operations, and also waste from the manufacture of organic chemicals, e.g., organic halides or amides, should be considered.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

The need for high temperature/pressure can cause hydrolysis to be a relatively energy-intensive process. A large portion of the energy needed often takes the form of electricity for heat or for steam generation. Steam may be used as a temperature (or pressure) source, and as a hydrolyzing agent.

- Production of fatty acids – The steam necessary to maintain the conditions detailed in the example of Section III is about 120 Btu/lb fatty acid produced. Electricity is required to preheat the fatty oil and water and to operate the pumps. Data are not available on the annual usage of the hydrolysis operation in isolation.

- Manufacture of titanium dioxide – The process described previously, using steam injection, requires about 1500 Btu steam/lb titanium dioxide formed. The total power for pumps and mixers is about 30 hp.

- Hydrolysis of cellulose (Refs. 16,17) – A projected analysis of the requirements for this process indicate that substantial amounts of energy may be required to hydrolyze paper refuse. Values on the order of 1000 Btu/lb refuse are reported.

One can readily see that the energy necessary for the various processes described can differ by orders of magnitude. Each operation has distinct needs, related to the chemistry of the particular hydrolysis – dependent on parameters such as temperature and pressure – and the size of the stream to be treated.

B. ENVIRONMENTAL IMPACTS

Hydrolytic reactions are capable of producing toxic by-products of any physical form. Parathion, cited earlier, is a case in which hydrolysis of a pesticide results in a hazardous compound remaining in solution. Undesirable gaseous products can be produced in high temperature operations or through entrainment when high pressure steam is used. Also, in the treatment of organic matter it is not uncommon to produce difficult to handle solid products, such as tars or sludges.

The addition of acid or base in hydrolysis results in the production of ions associated with these chemicals. Sulfate or chloride, are not generally considered hazardous; however, there are recommended limits for discharge, based primarily on taste. Common cations present after alkali addition may be sodium or potassium, both of which are non-toxic. In many instances, neutralization of the treated stream may be necessary to meet regulations concerning discharge pH.

C. ECONOMIC ANALYSIS

The capital investment and operating costs for hydrolysis depends largely on the individual process. The wide variety of equipment, e.g., hydrolysis towers, autoclaves, and open tanks, can generate large differences in capital estimates. The relationship between operating costs and energy requirements (discussed previously) accounts for a portion of the variability in these figures. The following examples will provide some indication of the cost differences to be encountered:

- Hydrolysis of polyurethane – General Motors estimates the capital cost for an installation with a feed of about 14 tpd of polyurethane would be about $275,000 (Ref. 14) -- about $20,000/daily ton. But a large part of this projected cost stems from non-hydrolysis related sections of the system.

- Hydrolysis of cellulose – An economic analysis for a plant capable of hydrolyzing 1000 tpd paper refuse was performed (Ref. 16). The capital investment is estimated at approximately $5-15 million dollars (about $5-15,000/daily ton), dependent upon operating parameters, e.g., temperature. Operating costs are about 0.75-1.5¢/lb; under certain conditions the oil used in generating heat could be almost one-third of the total operating cost. Due to economy of size, a decrease in capacity by a factor of 4 could increase the operating cost by as much as 70%.

Areas other than size in which costs (capital and operating) may differ include: materials of construction, raw materials (acids or alkalies), design for high temperature/pressure, ancillary equipment (such as scrubbers to prevent vapor emissions), and disposal or treatment (possibly recycle or resale) of hydrolysate.

As a common basis for cost analysis, the flow sheet example shown in Figure 4 has been designed and costed in a standard manner. The system selected for study is the hydrolysis of fatty oil since it has been characterized in prior sections. A description of the process is presented in Table 1. The fatty oil is analogous to a waste stream scheduled for treatment by hydrolysis. Table 2 is a summary of the economic analysis. The capital investment for a plant capable of handling 250,000 lb/day (125 tpd) is about $320,000 (about $2,500/daily ton); the operating cost is about 0.31¢/lb acid (approximately one pound of acid is produced per pound of oil). Credit for the product has not been included in the cost. The total cost for process steam is about 20% of the variable cost and more than five times that of electricity; the largest contributor to the cost is operating labor.

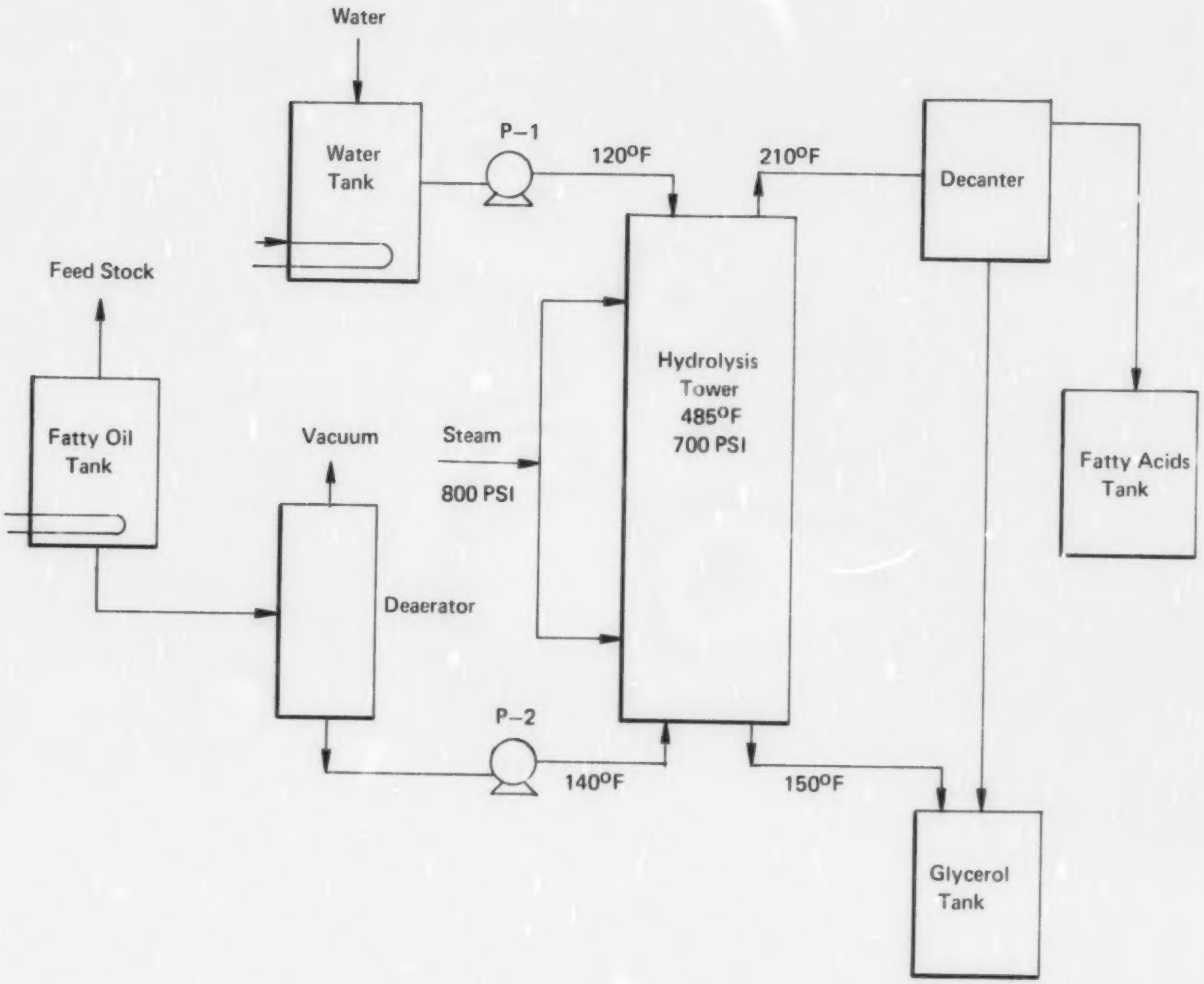

Water
Water Tank
P–1
120°F
210°F
Decanter
Feed Stock
Hydrolysis Tower
485°F
700 PSI
Fatty Oil Tank
Vacuum
Steam
800 PSI
Fatty Acids Tank
Deaerator
P–2
140°F
150°F
Glycerol Tank

FIGURE 4 COUNTERCURRENT HYDROLYSIS OF FATS

TABLE 1

REQUIREMENTS FOR COUNTERCURRENT HYDROLYSIS OF FATS

Basis:	250,000 lb/d Fatty Oil processed	
Equipment:	Hydrolysis Tower*	70 ft height x 3 ft diameter
	Water Tank (heated – 85°C)	20,000 gal
	Fatty Oil Tank (heated –96°C)	75,000 gal
	Deaerator	100 ft^3
	Decanter	80 ft^3
	Fatty Acids Tank	30,000 gal
	Glycerol Tank	30,000 gal
	Pumps	
	P-1	15 gpm
	P-2	25 gpm
Chemicals:	Fatty Oil	No cost
Utilities:	Steam	17,000 lb/d at 800 psi
	Electricity Two pumps	
	Process Water	18,000 gpd
Labor:	36 man-hours/day	

*Due to corrosivity of fatty acids, the hydrolysis towers, decanter, and fatty acids tank should be of 316 SS.

TABLE 2

ESTIMATED COST FOR HYDROLYSIS OF FATS

Basis: 250,000 lb/d Fatty Oil – 350 days/yr

Estimated Capital Investment: $320,000

	Annual Quantity	Cost Per Unit Quantity	Annual Cost ($)
Variable Costs			
Operating Labor (includes overhead & supervision)	12,600 M H	$12.00/M H	$152,000
Utilities			
Electricity	336x10^3 kWh	$0.02/kWh	$ 6,700
Water	6300x10^3 gal	$0.40/10^3 gal	$ 2,500
Steam	9500x10^3 lb	$4.00/10^3 lb	$ 38,000
Total Utilities			$ 47,200
Maintenance (@ 3% of Inv.)			$ 9,600
Total Variable Costs			$208,800
Fixed Costs			
Taxes & Insurance (@ 2% of Inv.)			$ 6,200
Capital Recovery (10 yrs @ 10%)			$ 52,000
			$267,000
Unit Cost – ¢/lb of Fatty Acid			$ 0.31

Source: Arthur D. Little, Inc., estimates.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Hydrolysis, as a commercial reaction, has been practiced for many years in different applications under a broad range of conditions. Although not in widespread use as a waste treatment process, it is a manufacturing process of demonstrated operability and reliability. The process can be conducted in simple equipment (batch-wise in open tanks) or in more complicated equipment (continuous flow in large towers). The handling of strong acids and alkalies requires care, but is not of undue concern. Performing reactions at high temperatures and pressures necessitates close control and monitoring of the process. However, the equipment and knowledge for such operations is readily available and presents no fundamental problem.

As a treatment process for hazardous wastes, hydrolysis can be applied to a wide variety of physical forms. It can be adapted to handle liquid, gaseous, or solid materials. With few exceptions, hydrolysis does not appear to be promising for disposal of inorganic materials. Its true strength lies in handling a wide range of aliphatic and aromatic organics, such as esters, ethers, carbohydrates, sulfonic acids, halogen compounds, phosphates, and nitriles.

The capital costs vary considerably depending on the equipment. Operating costs also vary as a result of the required severity of operating conditions. Higher temperatures/pressures lead to increased energy costs for heat by electricity and/or steam. Raw material costs are usually small, e.g., the use of sulfuric acid as a catalyst.

A potential disadvantage of hydrolysis is the possibility of undesirable reaction products; each case will of course need to be examined in detail as to economics as well as the acceptability of the products which result. It will frequently be necessary to conduct a preliminary laboratory scale investigation of the reaction, to determine the appropriate temperature, pressure, reaction time, and hydrolyzing agent (also concentration). The possibility of side reactions and the toxicity of any suspect products should also be studied.

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B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD

Organization	Contact	Comments
Dartmouth College Hanover, N.H.	Dr. Alvin Converse	Professor Converse is working on a process for hydrolyzing cellulose from paper refuse to glucose.
Dow Chemical Midland, Michigan	Robert Bailey	In a telephone conversation Bailey described the Dow crufomate process (no longer operating).
Ford Motor Research and Engineering Center Dearborn, Michigan	Dr. Lee Mahoney	Dr. Mahoney discussed the Ford process for hydrolyzing polyurethane foam with steam.
New Jersey Zinc Co. Gloucester City, N.J.	Foster Olsen Joseph O'Brien	N.J. Zinc practices hydrolysis of titanium sulfate in a batch – an example of inorganic hydrolysis.
Procter & Gamble Manufacturing Co. Quincy, Ma.	Clarence Stevens	P & G has a countercurrent hydrolysis tower for producing fatty acids from fatty oil.
U.S. Army Medical Bioengineering Lab. Fort Detrich, Md.	Dr. W. H. Dennis Dr. E. P. Meier	Dennis and Meier are involved in a study of the hydrolytic decomposition of various pesticides.

ION EXCHANGE

Prepared by

James R. Valentine

I. CONCLUSIONS AND RECOMMENDATIONS

Ion exchange is currently used for both general and selective removal of heavy metals and hazardous anions from dilute aqueous waste streams. Current waste applications include treatment of a wide variety of dilute wastewaters from electroplating and other metal finishing operations and recovery of materials from fertilizer manufacture. Promising applications include removal of cyanides from mixed waste streams, and use of new exchangers for selective removal of heavy metals without complete deionization.

II. PROCESS DESCRIPTION

A. BACKGROUND

Ion exchange involves the removal of ionic species, principally inorganic, from an aqueous or partially aqueous phase. The earliest applications of ion exchange (IE) were "water softening" – the substitution of sodium for calcium and magnesium in water, and the reverse substitution in sugar solutions to promote better crystallization. These applications were initiated in the late 1800's and early 1900's, using natural and synthetic zeolites (aluminosilicate minerals). Synthetic ion exchange resins were discovered in the late 1930's and were developed rapidly, particularly after World War II. Applications broadened rapidly into diverse areas such as hydrometallurgy (separations of uranium elements and the rare earth series, for example), and waste treatment (recovery and removal of chromium species). Deionization applications, especially for high quality process water (nuclear power and conventional steam generators) is probably still the most widespread application.

B. UNDERLYING PRINCIPLES

In simplest terms, ion exchange may be thought of as the reversible interchange of ions between an insoluble, solid salt (the "ion exchanger") and a solution of electrolyte in contact with that solid. As an example, a cation exchange material (designated R^-) having a cation (N^+) associated with it can react with a solution of an electrolyte (M^+X^-) as shown below:

$$M^+ + X^- + R^-N^+ \rightleftharpoons R^-M^+ + N^+ + X^- \qquad \text{(Eq. 1)}$$

The direction (forward or reverse) and extent of the reaction are governed by the relative insolubilities of the insoluble salt(s) that can be formed [i.e., MX, NX, RM, RN] and by the equilibrium constant for the reaction,

$$K_{eq} = \frac{[RM]\,[N^+]}{[RN]\,[M^+]} \qquad \text{(Eq. 2)}$$

where [RM] and [RN], and $[N^+]$ and $[M^+]$ represent the concentrations of the cations in the ion exchange material, and in the solution, respectively. K_{eq} is constant for any given set of R^-, M^+, and N^+ for solution concentrations up to approximately 0.1 mol/liter, but may vary somewhat above that point. As with similar equilibrium reactions, changes in either $[M^+]$ or $[N^+]$ will result in a change in the equilibrium position, or extent, of reaction.

C. OPERATING CHARACTERISTICS

1. Feed Streams

Ion exchange is applicable to aqueous streams and to single-phase streams which are partially aqueous, such as ethylene glycol-water mixtures. It is also applicable to the water phase from aqueous slurries (scrubber slurries, for example), provided that all suspended solids, which would plug the exchange bed, are removed prior to exchange.

As examples of general applicability, ion exchange can be used to remove and/or concentrate the following classes of chemicals.

- Inorganic:
    - All metallic elements when present as soluble species, either cationic or anionic;
    - Anions such as halide, sulfate, nitrate, cyanide, etc.;
    - Neutralization of acidity or alkalinity, particularly useful for controlled neutralization by means of weak base and weak acid resins.
- Organic (water soluble and in general ionic):
    - Acids such as carboxylics, sulfonics and some phenols, at a pH sufficiently alkaline to give the ions;
    - Amines, when the solution acidity is sufficiently acidic to form the corresponding acid salt;
    - Anionic and cationic species such as quaternary amines and alkylsulfates, frequently used as detergents.

Generally, if a species known to be exchangeable in aqueous solution can be scrubbed, dissolved or otherwise extracted from another form or phase (gaseous, liquid or solid), then ion exchange can be used to concentrate that species.

The upper concentration limit for the exchangeable ions for efficient operation is generally 2500 mg/l, expressed as calcium carbonate (or 0.05 equivalents/l). This upper limit is due primarily to the time requirements of the operation cycle. A high concention of exchangeable ion results in rapid exhaustion during the service cycle, with the result that regeneration requirements, for both equipment and of the percentage of resin inventory undergoing regeneration at any time, become inordinately high.

The DESAL process (Rohm and Haas Company), a fixed-bed process for deionization (Section III-B), is claimed to operate efficiently with electrolyte concentrations up to 4000 mg/l (Ref. 21). Continuous countercurrent operation offers advantages at high concentrations in that the resin flow (which is countercurrent to solution flow) can be relatively rapid, within certain limits, to keep up with rapid exhaustion (Refs. 7,30,33).

There is also an upper concentration limit (around 10,000-20,000 mg/l), which is governed by the properties of the ion exchangers themselves, in that the selectivity (preference for one ion over another) begins to decrease as the total concentration of dissolved salts (ionic strength) increases (Ref. 1).

Synthetic resins can be damaged by oxidizing agents and heat. In addition, the stream to be treated should contain no suspended matter or other materials which will foul the resin and which cannot be removed by the backwash operation. Some organic compounds, particularly aromatics, will be irreversibly absorbed by the resins, and this will result in a decreased capacity, as for example in the case of electroplating bath additives (Ref. 35).

2. Process Operations

a. Process Chemistry

In the customary mode of usage, the ion exchanger is contacted with the solution containing the ion to be removed until the active sites in the exchanger are partially or completely used up ("exhausted") by that ion. The exchanger is then contacted with a sufficiently concentrated solution of the ion originally associated with it to convert ("regenerate") it back to its original form. For the general exchange

$$M^+ + X^- + R^-N^+ \rightleftharpoons R^-M^+ + N^+ + X^-,$$

these steps are:

$$R^-N^+ + M^+ \longrightarrow R^-M^+ + N^+, \qquad \text{(Eq. 3)}$$

which is termed the "exhaustion," "service" or "loading" step, and

$$R^-M^+ + N^+ \text{ (high concentration)} \longrightarrow R^-N^+ + M^+, \qquad \text{(Eq. 4)}$$

which is termed the "regeneration" step. Since $[N^+]$ is higher in the regeneration step than in the service step, the solution volume for regeneration can be smaller, and consequently $[M^+]$ will be higher in the regeneration solution

An alternative route for regenerating the ion exchanger involves a third ion (frequently a hydrogen ion in cation exchange) to give the corresponding form of the exchanger which can then be converted to the desired salt as shown below:

$$R^-M^+ + H^+ \longrightarrow R^-H^+ + M^+ \qquad \text{(Eq. 5)}$$

$$R^-H^+ + N^+OH^- \longrightarrow R^-N^+ + H_2O \qquad \text{(Eq. 6)}$$

Such a sequence might be desirable in a case where H^+ was a much more effective regenerant than N^+, but where the release of H^+ into the solution being purified would be undesirable.

Thus, ion exchange provides a mechanism for removing an undesirable ion from a stream, and for transferring that ion, at a higher concentration than before, to another aqueous stream.

It is important to remember that this process is an exchange rather than a direct removal of ions, and thus does not alter the total molar equivalent concentration (i.e., total chemical equivalents of ions) of salts in the solution. In order to lower the total salt concentration in the solution (in equivalents per liter) it is necessary to perform a sequential exchange of cations and anions for hydrogen ion and hydroxyl ion respectively, thereby exchanging the salt for water. This "deionization" sequence for the salt M^+X^- is thus:

$$M^+X^- + R^-H^+ \qquad R^-M^+ + H^+X^- \qquad \text{(Eq. 7)}$$

$$H^+X^- + R^+OH^- \qquad R^+X^- + H_2O \qquad \text{(Eq. 8)}$$

The ion exchange process works well with cations (including, of course, the hydrogen ion) and anions, both inorganic and organic. However, the organic species frequently interact with the exchangers (particularly the organic resins) via both absorption and ion exchange reactions, often necessitating the use of extremely high regenerant concentrations and/or the use of organic solvents to remove the organics. Consequently, most of the applications of ion exchange of interest to this study have involved inorganic species.

The relative insolubilities (or, better, the stability constants) of the possible salts that can be formed by the ions and the exchangers also enter into the K_{eq} and thus affect the extent of the exchange reaction. There are a variety of different cation and anion exchangers which form salts of more or less different stabilities with a particular ion. Thus, knowledgeable choice of a particular ion exchange material will often allow selective separation of one ion in solution from another, and afford selective removal of an undesirable ion from a number of innocuous ones.

As a general rule, ions with a higher charge will form more stable salts with the exchanger than those with a lower charge, and hence polyvalent species can frequently be selectively removed from a solution of monovalent ones.

b. Modes of Operation

In carrying out ion exchange reactions in a column or bed operation (as opposed to a stirred batch operation, which is occasionally used in chemical processing), there are four operations carried out in a complete cycle:

- service (exhaustion)
- backwash
- regeneration
- rinse

The service and regeneration steps have been described above. The backwash step is one in which the bed is washed (generally with water) in reverse direction to the service cycle in order to expand and resettle the resin bed. This step eliminates channeling which might have occurred during service and removes fines or other material that may be clogging the bed. The rinse step removes the excess regeneration solution prior to the next service step.

There are three principal operating modes in use today: cocurrent fixed-bed, countercurrent fixed-bed and continuous countercurrent. Flow diagrams for these processes are shown in Figure 1, and a brief summary comparison is given in Table 1.

TABLE 1

COMPARISON OF ION EXCHANGE OPERATING MODES

	Cocurrent Fixed Bed	**Countercurrent Fixed Bed**	**Countercurrent Continuous**
Capacity for high feed flow & conc.	Least	Middle	Highest
Effluent Quality	Fluctuates with bed exhaustion	High, minor fluctuations	High
Regenerant and rinse requirements	Highest	Somewhat less than cocurrent	Least, yields most conc. regenerant waste
Equipment complexity	Simplest; can use manual operation	More complex; automatic controls for regeneration	Most complex; completely automated
Equipment for continuous operation	Multiple beds, single regeneration equipment	Multiple beds, single regeneration equipment	Provides continuous service
Relative Costs (per unit volume)			
Investment	Least	Middle	Highest
Operating	Highest chemicals & labor; highest resin inventory	Less chemicals, water & labor than cocurrent	Least chemical & labor; lowest resin inventory

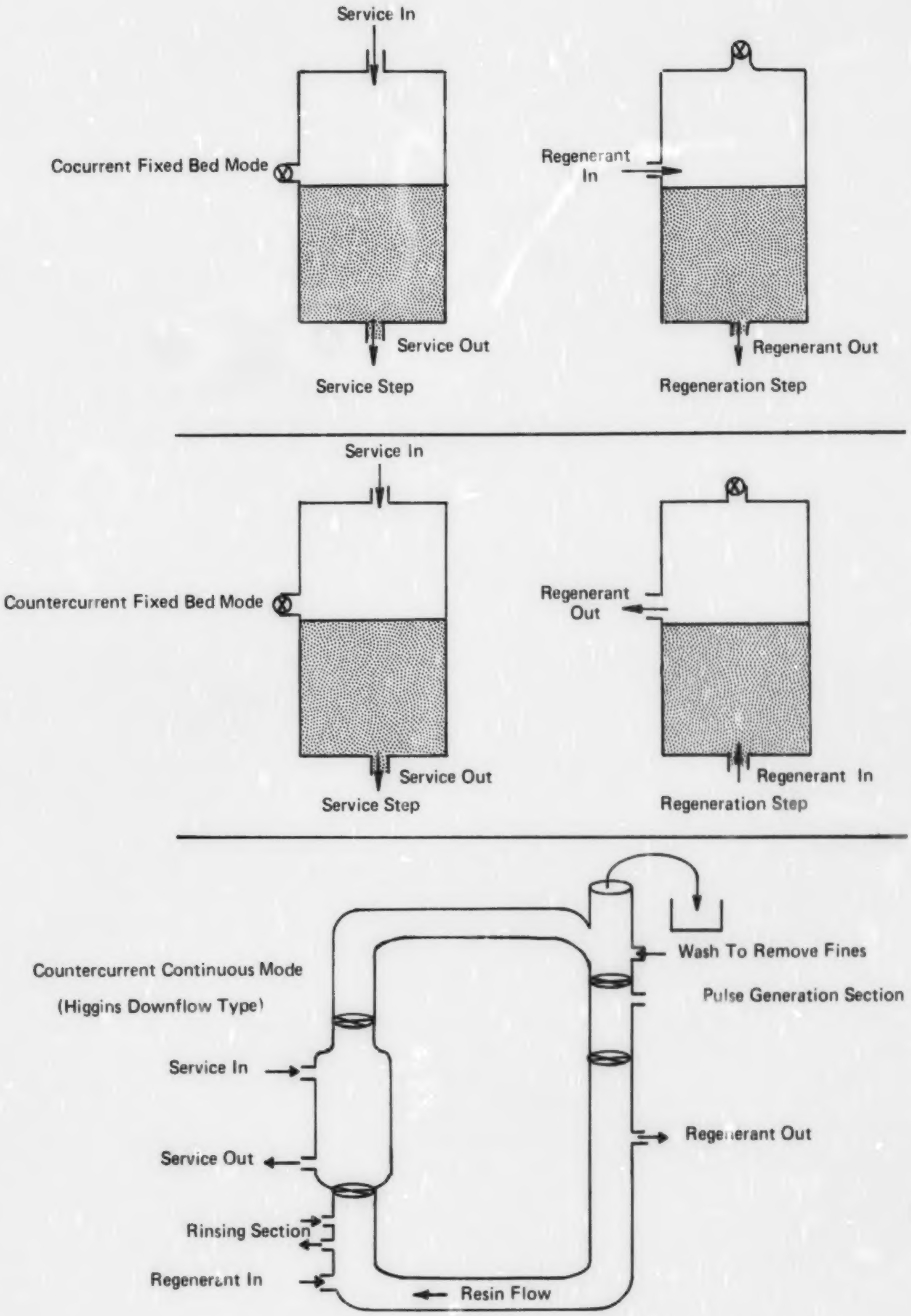

Service In
Cocurrent Fixed Bed Mode
Service Out
Service Step
Regenerant In
Regenerant Out
Regeneration Step
Service In
Countercurrent Fixed Bed Mode
Service Out
Service Step
Regenerant Out
Regenerant In
Regeneration Step
Countercurrent Continuous Mode
(Higgins Downflow Type)
Service In
Service Out
Rinsing Section
Regenerant In
Resin Flow
Wash To Remove Fines
Pulse Generation Section
Regenerant Out

FIGURE 1 OPERATIONAL MODES FOR ION EXCHANGE

Most ion exchange installations in use today are of the fixed-bed type, with countercurrent operation coming more into favor, especially for removal (polishing) of traces of hazardous species from the stream prior to reuse or discharge (Refs. 23,27).

In order to minimize regeneration chemical requirements (i.e., to make most efficient use of regenerant), many fixed-bed installations use a technique termed "staged," or "proportional," regeneration. The first part of the regeneration solution to exit from the ion exchange bed is the most enriched in the component being removed; the concentration of that component decreases in succeeding portions of the exiting regeneration solution. In staged regeneration, the solution is divided (generally in separate tanks) into two or more portions. The first portion through the bed is "discarded" (i.e., sent for subsequent treatment), while the second and succeeding portions (less rich in the species being removed) are retained. On the next regeneration cycle, the second portion from the preceding cycle is passed through the bed first (and then "discarded"), followed by the succeeding portions, the last of which is a portion of fresh regenerant. In this way, regenerant utilization can be maximized.

There are many firms who design, manufacture and install fixed-bed ion exchange systems. A representative, but not exhaustive, listing of such firms is given in Section VI.

Continuous countercurrent ion exchange systems in a variety of configurations have been offered on the commercial market over the past few years (Refs. 6,7,9-11, 23,27,30-33,50). Included in these are the *Higgins*-type systems (Refs. 7,30-33), the *Asahi*-type, the *Graver C.I. Process* (Refs. 9,10), the *Permutit* process (Ref. 50), and a fluidized moving-bed system (Ref. 11). Of these, only the *Higgins*-type is currently being marketed by *Chemical Separations Corp.* (Refs. 23,27,33), with the other types being discontinued and even replaced by fixed bed units in some cases (Ref. 33). Problems have included inefficiency stemming from the need for close flow control for upflow operation, high resin attrition, and the multitude of mechanical problems that might be expected from such complex solids-handling systems (Refs. 23,27,31,33).

One other mode of ion exchange uses the so-called "powder resins." The ion exchange resins are prepared as fine powders (generally less than 400 mesh) and are applied in relatively thin layers (because of the high impedance to flow) to a filter support (plate, tubular filter, etc.). The fine particles are extremely efficient for ion exchange (large surface area and little intra-particle diffusion), but are generally not regenerated because of the handling, flow and pressure problems. This mode has found extensive use as disposable polishing units in the nuclear power industry (Ref. 34), and it might have analogous application in polishing effluents resulting from the treatment of extremely hazardous wastes.

3. Output Streams

In the usual modes of operation (Table 1), the ion exchange process yields two liquid streams:

- a large-volume purified product stream depleted in the species being removed, and
- a small volume solution of used ("spent") regenerant containing a high concentration of the species removed.

The feed/regenerant ratio can be as much as 50/1 or higher for treating very dilute feed streams.

The ion exchange system is virtually always designed so that the purified product stream can be recycled, used in another process, or discharged without further treatment.

The spent regenerant must be treated to remove or detoxify the species it contains, and since that species is at a much higher concentration than in the original stream, such treatment is frequently easier and/or more economical than it would have been prior to the ion exchange treatment.

In some cases the spent regenerant containing the species it has removed and concentrated can be recycled back to a process without further treatment. This is done with chromium and nickel in some electroplating operations (Refs. 4,23,27,29,36) and with chromium in some recently developed processes for treating cooling tower blowdown (Refs. 21,33,39,40).

For conventional ion exchange in waste treatment, the use of solid ion exchange materials affords three advantages over such competitive separation processes as liquid ion exchange and reverse osmosis.

- In processing small quantities (batches) of waste streams, the partially exhausted resin need not be regenerated after each batch but can be held in the "partially loaded" state for use with subsequent batches of waste.
- For the ultimate disposal of extremely hazardous wastes that are strongly bound to the ion exchanger (i.e., would not desorb under any expected conditions), the loaded resin can be encapsulated, or otherwise contained, and disposed of directly. This approach has been used in handling radioactive wastes (Refs. 16,34).

- For the transport of extremely hazardous species (for example, residues from heavy metals such as thallium) between processing operations, particularly if those operations are widely separated physically or at different sites, the use of loaded solid ion exchangers may be more acceptable from an environmental standpoint than transport in solution because of the diminished hazards in the event of a spill.

D. EQUIPMENT AND MATERIALS

1. Equipment

Fixed-bed ion exchange operations are straightforward systems, requiring a cylindrical ion exchange bed, tanks for solution storage, and pumps. The choice of materials is governed by the chemical environment.

Continuous ion exchange systems much more complex, requiring solids handling equipment and more intricate control systems. Apparently only one company (Chemical Separations Corp.) has been truly successful in the design and fabrication of continuous ion exchange systems, and it should be consulted if the use of such a system is contemplated.

2. Ion Exchange Materials

The classes of materials that are in use or that have been proposed for use as ion exchange materials include inorganic crystals (both natural and synthetic) and synthetic organic resins. This last category is by far the most important for general ion exchange usage.

Three important parameters for ion exchange materials by which the exchangers can be selected and compared, and from which approximate exchanger and chemical requirements can be determined, are functionality, exchange capacity, and selectivity. Functionality refers to the kinds of ions (cations, anions, selected groups) that are exchanged; exchange capacity is a measure (generally in milliequivalents per gram, or per milliliter of resin) of the total uptake of a specified ion; selectivity refers to the preference for one kind of exchangeable ion over another, expressed as a ratio similar to K_{eq} in Eq. 2 (Section II-B) at unit concentrations of $[M^+]$ and $[N^+]$.

a. Synthetic Ion Exchange Resins

A variety of cation and anion exchangers have been prepared by adding appropriate functional groups (exchange sites) onto solid particles (usually beads) of polymeric materials. In some resins, the functional groups are introduced prior to or during the polymerization step. Most of the resins now offered commercially are either styrene-divinylbenzene copolymers or acrylate-methacrylate copolymers.

Earlier ion exchange resins were prepared from phenol-formaldehyde ("Bakelite") and related polymers; however, these materials were inferior to the present ones in stability, variety, and capacity, and only a few specialized ones are now available.

In the past, styrene-divinylbenzene materials suffered from rather large volume changes ("swelling") when cycled between different ionic forms. Newer methods of preparation and materials have now resulted in a variety of "macroreticular" resins, which combine a rigid polymer framework with a high exchange capacity and suffer only minor swelling.

Some of the more common reactive groups offered are listed below:

Reactive Group	**Exchangeable Ions**
strong acid (sulfonic)	cations in general
weak acid (carboxylic)	cations in general
weak acid (phenolic)	cesium and polyvalent cations
strong base (quaternary amine)	all anions, esp. used for anions of weak acids (cyanide, carbonate, silicate, etc.)
weak base (tertiary and secondary amine)	anions of strong acids (sulfate, chloride, etc.)
chelating (varied, may be imino-diacetate or oxime groups)	cations, especially transition and heavy elements

Differences in the particular starting materials and preparation route frequently give rise to differences in handling properties, stability and reaction kinetics between resins that have the same polymer backbone, functional groups, and exchange capacity. Hence it is important to test a variety of resins for a particular application. A reasonably comprehensive listing of older types of resins is given in Perry's Handbook (Ref. 43). For more up-to-date information, the various resin manufacturers should be contacted directly.

The synthetic resins are generally stable to strong acids and bases, but suffer irreversible damage from oxidizing agents, high temperature, and radiation (Ref. 1).

b. Inorganic Ion Exchangers

Both naturally-occurring and synthetic zeolites (aluminum silicate minerals) have been used as cation exchangers. The majority of these materials are stable only over a narrow pH range (neutral) and are somewhat fragile. A major use of these materials is water softening. Newer synthetic materials such as zirconium phosphates have improved physical and chemical (acid range) properties (Ref. 1).

These materials are never used in continuous operation because their geometry (non-spherical), density and fragility preclude effective solids handling operations.

The inorganic exchangers are less affected by oxidants, heat and radiation than are the synthetic resins, and consequently have found use in the processing and disposal of radioactive wastes (Refs. 2,4).

c. Modified Natural Organic Materials

A variety of natural materials have been proposed and demonstrated for ion exchange, including sulfonated coals, sulfonated nut shells, and modified cottons (Refs. 1,25). For example, peanut hulls were used to remove traces of heavy metals from solution (Ref. 25). While none of these has been used recently in a large scale process, they may find some use in a single pass disposal system.

d. Ion Exchange Liquids

The so-called liquid ion exchange process (often termed "solvent extraction") in which the ion exchanger is a water-insoluble liquid, resembles a liquid/liquid extraction process in operation rather than conventional ion exchange; this technique is the subject of a separate report.

Recently, there have been reports of impregnating beds of synthetic resin with liquid ion exchangers to produce an exchange material that could be handled via conventional ion exchange operations and could have some important advantages in selectivity (Refs. 48,49).

III. APPLICATIONS TO DATE

A. PRINCIPAL CURRENT APPLICATIONS

The first use of ion exchange was in water softening. Today ion exchange is utilized widely in a number of industrial areas. A brief overview of major applications will indicate what information of use to hazardous waste processing might be gained from each area.

1. Deionization

Industrial deionization, which in its broadest meaning includes processes yielding products ranging from potable water to boiler water for steam production, is by far the most frequent application of ion exchange, apart from domestic softening. (This latter area involves only exchange of sodium for calcium and magnesium under ambient conditions and affords little information for waste treatment application.) Deionization applications generally operate on a relatively clean feed, at worst brackish water, which has been pretreated where necessary to remove most foulants. The product must often meet stringent quality standards, particularly for newer boiler-water applications. Information on reliability of equipment operation can be had from the manufacturers of ion exchange equipment (Section VI). Since this application is generally a steady-state operation, such information can be used to set upper limits on the reliability of equipment, particularly for newer modes of operation such as continuous countercurrent. (Ref. 31).

2. Electroplating Wastewaters and Resins

Ion exchange is used extensively in the electroplating industry, especially in large installations, to remove ionic impurities from rinse water enabling re-use of the water and for further treatment of the impurities prior to disposal or recycle (Refs. 4,23,27,29,36). Some new installations are being designed to meet the "zero discharge" requirements anticipated in the near future. In certain cases, the electroplating bath itself may require a cleanup treatment, but this is not usually done directly via ion exchange.

Ion exchange is used most frequently in combination with other techniques such as reverse osmosis or precipitation to yield an optimal solution for the particular application; in general, ion exchange is employed as the final or "polish" step, particularly if the stream to be treated contains higher concentrations of the species to be removed than can be easily handled by this process (Refs. 23,27-29,36). Small-scale portable (skid-mounted) units incorporating carbon adsorption filters with series and parallel beds of appropriate ion exchange resins (cation, anion and chelating) have been marketed for cleaning up individual rinse tanks on-site (Refs. 22,29). These units are regenerated separately off-site.

The rinse solutions from electroplating operations are for the most part fairly dilute mixtures of components that might well be found in the effluent from a hazardous waste treatment facility – chromium (VI and III), cyanide, nickel, etc. Thus information on ion exchange applications in this area may well be directly applicable to waste treatment processes involving reclamation of hazardous components and rectification of water prior to discharge. The equipment used is virtually all simple batch-type and operation is often intermittent. Information on equipment and material reliability under conditions approximating batch waste disposal should be available from the users.

Some general applications of ion exchange in handling such rinse waters are discussed below.

Chromium (VI) is removed from plating rinses by contact with a strong base ion exchanger (hydroxide form) after neutralization of the rinse stream to pH 8-9. The chromium (as chromate) is removed, and the resin is regenerated with sodium hydroxide solution. In most installations the rinse water is also treated with a cation exchange (acid form) to yield deionized water for recycle to the rinse tanks. The spent regeneration solution, which contains sodium chromate and sodium hydroxide, is neutralized with sulfuric acid and then treated with a cation exchanger to give chromic acid for recycle to the plating bath (Refs. 23,28,36).

The countercurrent fixed-bed mode of operation is often used because the extra "polishing" achieved over cocurrent flow is needed to assure meeting the low limits for recycle or discharge of chromium (Refs. 23,27).

Treatment of metal-cyanide complexes is another application. Although these complexes are treated directly to destroy the cyanide, the destruction is easier and more economical if most of the complexes have been destroyed and the metals removed. To "break" the complexes, the solutions are treated sequentially, first with a cation exchanger to "break" the complexes and then with an anion exchanger to take up the liberated cyanide as shown below.

$$M(CN)_2^+ + 2R^-H^+ \rightleftharpoons R_2^- M^{++} + 2HCN$$

$$2HCN + 2R^+OH^- \rightleftharpoons 2R^+CN^- + 2H_2O$$

The potential for release of toxic HCN is minimized by directing the cation exchange effluent immediately to the anion exchanger.

In order to isolate the cyanide completely for most economical destruction and to avoid premature exhaustion of the anion resin by other anions such as chloride and sulfate, commercial systems utilize a second anion exchanger of the weak base type interposed between the other two to remove the chloride and sulfate, but allow the cyanide to pass through (Refs. 2,23).

$$R_3N \text{ (weak base)} + \begin{Bmatrix} H^+Cl^- \\ H^+SO_4^= \end{Bmatrix} \longrightarrow \begin{Bmatrix} R_3N^+HCl^- \\ R_3N^+HSO_4^= \end{Bmatrix}$$

A number of systems of this type are reported to be in use at this time (Refs. 21,23). In some designs the anion exchangers are combined in one column with a layer of the weak base resin above the strong base one (Ref. 23). Upflow (countercurrent) regeneration with sodium hydroxide gives complete conversion of the lower bed so that cyanide removal will be maximized.

Small-scale units have been marketed for the treatment of individual rinse tanks (100-2500 gallons) in plating shops (Refs. 22,29).

3. Mixed Waste Streams

In the general metals finishing business it is quite common to have a single solution waste handling system that can only be described as "mixed waste." Obviously a variety of waste treatment schemes would be needed in order to be able to treat mixtures with constituents including suspended metal particulates, oil and grease, chromium (III and VI), iron phosphate, cyanide, zinc, etc. A common thread among most treatment schemes is the frequent use of some sort of ion exchange step for final treatment before re-use or discharge (Refs. 20,21,23,27,28,29). The major amounts of materials in mixed wastes are removed or destroyed by precipitation, filtration, or a membrane separation and ion exchange is used as the "polishing" step.

The following Treatment Systems are examples:

Waste	Treatment Sequence	Started	References
Metal finishing (300,000 gal/day) Singer Co.	Oil sep.; reverse osmosis; conc. product to ion exchange; regenerant treated to destroy cyanide and then discarded	March 1976	27
Mixed plating rinses Tinker AFB (Okla.)	sep'n; some precipitation; ion exchange to remove cyanide and some metals	Recently	23
Metal finishing (8,000,000 gal/day) Germany	Neutralization w/acids; precipitation and filtration; ion exchange all water for re-use	Mid 1960's	20

4. Other Metal Finishing Streams

In addition to treating dilute aqueous streams, ion exchange is being used to remove low concentrations of undesirable impurities from relatively highly concentrated aqueous streams. The object of treatment in most cases is to recycle or reclaim the active materials while ridding the bath of unwanted impurities. Frequently ion exchange is the sole separation step, with other post-treatment steps being carried out on the spent regenerant solution.

Minor concentrations of cations such as iron, aluminum and chromium (III) are removed from chromic acid plating bath liquors via cation exchange, after dilution of the chromic acid content of the liquor from 250 g/l down to 100 g/l (Refs. 14,44). The dilution is necessary in order to obtain efficient exchange and to minimize oxidative damage to the sulfonated styrene-divinyl benzene resins used.

Another large-scale application is for the removal of aluminum from strong phosphoric acid/nitric acid solution used for cleaning ("bright dipping") aluminum metal (Refs. 33,36,45). The phosphoric acid that has become contaminated with dissolved aluminum phosphate salts from dissolution of metal during the treatment is diluted with rinse tank water to give a 40% phosphoric acid solution which is then subjected to cation exchange to remove the aluminum. The purified phosphoric/nitric acid mixture is then evaporated to give concentrated acid for recycle to the process. The resin is regenerated with sulfuric acid to give aluminum sulfate. Both fixed bed and continuous countercurrent installations are in operation (Ref. 33).

In both of the above cases, neither of the main substances is a strong electrolyte – i.e., both are only partly ionized; thus ion exchange is effective, since the minor components being removed are ionized.

This area may provide useful information on continuous ion exchange operations, and resin behavior under somewhat rigorous reaction conditions. Liquid ion exchange processes have also been proposed and utilized for similar operations (Refs. 3,38), and the comparison may be useful.

5. Applications in Hydrometallurgical Processing

Ion exchange has been used for recovery of valuable metals such as copper, molybdenum, cobalt and nickel, especially from dilute leach liquors from tailings or dump piles (Ref. 41). Liquid ion exchange has been more widely used in general in the areas; however, the advent of new, more-selective resins coupled with the increased cost of solvent losses (which are at present unavoidable in liquid ion exchange) is resulting in increased interest in the solid exchangers (Ref. 41).

Uranium processing and extraction is an active field for both solid (Refs. 13,17,41,42) and liquid ion exchange (Ref. 42). Solid ion exchange is being used for recovery of carbonate leaches from in situ uranium mining in Texas (Ref. 41).

Information in this field may have direct application to treatment of certain waste streams, and should be useful for comparison of solid and liquid ion exchange.

6. Removal and Isolation of Radioactive Wastes

A great deal of work has been reported on removal of traces of radioactive species from solutions of various kinds. Of particular interest to waste treatment is a summary of the performance of ion exchange systems in operational nuclear power plants, which indicated that the severe conditions of radiation and heat resulted in attrition rates higher than those expected in non-nuclear service. Even under these conditions, operating capacity varied from 50 to 75% of the theoretical (Ref. 34).

Experience over long service lives in nuclear operations may provide some useful information on the long term behavior of ion exchange materials. Equipment reliability is normally extremely good in nuclear service, having been deliberately designed that way because of the extreme necessity to avoid trace ion leakage and equipment downtime.

7. Other Streams Containing Inorganic Species

Ion exchange is used for the removal and recovery of ammonium nitrate from fertilizer manufacturing waste streams by means of continuous countercurrent systems (Refs. 32,33). Information on the use and reliability of this mode of operation may be of use in waste treatment.

8. Treatment of Streams Containing Organic Materials

Ion exchange processes have been employed at one time or another to remove and/or separate organic materials and inorganic salts from mixtures of industrial origin.

The DESAL process (weak base resin in bicarbonate form, followed by weak acid resin in acid form) was used to treat "sour water" condensate from a petroleum refinery and achieved the results shown below (Ref. 5).

	Before (mg/l)	After (mg/l)
Total dissolved solids	1310	210
H_2S	1150	<3
NH_3	390	5
phenol	365	<20

These data indicate that certain types of organic compounds can be removed, together with inorganic salts.

As illustrated above, ion exchange has been used to remove odorous species, such as hydrogen nilfide and amines, which can be made ionic by a shift in pH.

In another kind of ion exchange separation, termed "ion exclusion," aqueous mixtures of sodium chloride and glycerol have been separated to yield aqueous solutions of the components (Ref. 18), and highly saline liquid wastes from food processing have been desalinized by this method (Ref. 19). In this type of separation, the ion exchanger employed is a cation exchanger in the form of the predominant inorganic salt, in these cases sodium. When the mixture is contacted with the ion exchanger, the presence of the sodium cation in the resin causes the sodium in the solution to be excluded from the resin (the chloride is also excluded in order to maintain the "charge balance" with sodium) while the non-ionized organic material can penetrate into the resin. Thus when the mixture is caused to pass through a bed of the exchanger, the solution is enriched somewhat in sodium chloride while the organic material is retarded slightly by diffusion into and out of the resin. Complete separation can be accomplished by use of multiple beds or multiple passes through the same bed (Ref. 18).

Thus ion-exchange processes have some utility in removing and separating both organic and inorganic species. There are competitive absorption and membrane processes, such as reverse osmosis, that generally perform better than ion exchange for such separations.

B. POTENTIAL APPLICATIONS IN WASTE TREATMENT

There are a number of new developments in ion exchange at the pilot and laboratory scale in the areas of chromium recycle, metal pickling waste treatment, cyanide removal and novel ion exchange resins.

1. Recovery of Chromium from Cooling Tower Blowdown

Both continuous countercurrent (Refs. 11,46) and fixed-bed (Ref. 41) systems have recently been proposed for recovery (and recycle) of chromium from cooling tower blowdown waters, and two systems have been run in pilot scale (Refs. 33,41).

The *Chem Seps* continuous unit (Ref. 46) uses a mixed-bed (cation and anion unstated composition) to remove both Chromium VI and Chromium III, as well as zinc. Chromates are eluted with sodium hydroxide and can be returned to the tower feed; Chromium III and zinc are eluted with acid and removed.

The *Rhom and Haas* fixed bed unit (Ref. 41) utilizes a weak base resin operating in the acid form to load the chromate, elution with sodium hydroxide for removal of the acid chromate and regeneration with sulfuric acid before the next cycle. If removal of Chromium III and zinc are needed, then additional beds utilizing a sodium form weak acid resin can be used.

Comparative cost estimates on the two systems are discussed in Section IV-C.

2. Treatment of Metal Pickling Wastes

A recently-developed system for the removal of ferrous salts (iron II) from steel pickle liquors containing from 1% to 10% of the salts in 5% to 20% sulfuric or hydrochloric acid employs cation exchange (acid form) in a continuous countercurrent mode (Ref. 37). The cleaned acid, returned to full strength from the exchange, is recycled to the process. The resin is regenerated with warm 22% nitric acid, which results in complete oxidation of the iron to the ferric (iron III) state during removal. Hydrolysis of the resulting ferric nitrate solution yields ferric oxide (Fe_2O_3) and nitric acid for recycle to regeneration. This process has been run on the pilot scale, and a demonstration scale operation will be run soon (Ref. 33). Very little resin degradation was found during the pilot runs.

An analogous system for copper pickle liquors has been developed using a weak acid cation exchanger; however, no particulars were available (Ref. 33).

The iron content is so high that the volume of liquors is approximately the volume of resin needed to take up the iron. In this case, continuous countercurrent operation has two advantages over fixed bed: less dilution of product with continuous mode because of effective rinsing and close control of the rinse water/product interface associated with rinsing; and much lower regeneration equipment and resin inventory requirements. A fixed-bed system would have most equipment and resin in the regeneration cycle at any time.

The pickling liquor application indicates that ion exchange can be used in selected high concentration situations, and may in some cases be an alternative to liquid ion exchange separation processes.

3. Removal of Cyanides from Aqueous Waste Streams

Now at the laboratory stage is a new approach to using ion exchange for the removal of cyanide. This involves deliberate conversion to ferrocyanide ion and selective removal of ferrocyanide in the presence of other salts and organics using a weak base resin in an acid salt form (Ref. 47).

The waste stream is brought to a pH of 9 to 11, and excess ferrous (iron II) sulfate is added to give ferrocyanide. Any excess ferrous ion precipitates as the hydroxide at this pH, and is removed by suitable means such as settling. The solution is acidified to a pH between 4 and 7, and is contacted with the ion exchanger, a macroreticular, acrylic, weak base resin in the acid salt form. The resin is very selective for weak acids such as ferrocyanide and does not remove anions such as sulfate and chloride, metal cations, and most organics. Treatment of the loaded resin with dilute sodium hydroxide solution yields a concentrated solution of the ferrocyanide which can be further treated for destruction or detoxification.

The resin is treated with dilute acid to convert it to the acid form in preparation for the next cycle.

The cyanide complexes of copper, zinc and nickel, which may be present in waste streams, are less stable than ferrocyanide and would be expected to respond to the treatment process.

When tested on a waste stream containing 2% inorganic salts and a chemical oxygen demand of approximately 400 mg/l, the process reduced the total cyanide concentration from 1 mg/l to less than 0.1 mg/l.

The process is relatively straightforward and could be of significant value in removing and concentrating cyanides from streams that contain high concentrations of substances (particularly organic materials) that would interact with and result in excessive consumption of the reagents most commonly used for the destruction of cyanide, such as hypochlorite.

4. New Ion Exchange Materials

A number of new ion exchange resins have been tested on the laboratory and pilot scale for general use, and these should be given more thorough testing for waste treatment. Many of these resins are of the macroreticular type, and are thus less subject to fouling and loss of capacity than older materials, a property which is of extreme importance in the treatment of wastes where foulant materials such as oils and soaps commonly may be present.

A new chelating resin, Amberlite XE-318, from *Rohm and Haas*, is particularly interesting since it is highly selective for a variety of transition metals, has a wide operational pH range (above pH 2), is more resistant to abrasion than previous resins of this type, and is significantly less expensive than previous resins (Refs. 21,22).

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

The energy requirements for ion exchange are quite low, consisting primarily of electricity for pumping; the driving force for the process is chemical. The ADL cost example and a previous study of the deionization of water puts power costs at 2-5% of the total operating costs.

B. ENVIRONMENTAL IMPACTS

Ion exchange is a solution (aqueous) phase process. The dilute, purified product stream can be suitable for discharge to sewers. The concentrated regeneration stream requires further treatments for recovery and/or safe disposal of its components.

Emissions to air will be essentially zero.

Emissions to water will be significant only if the regenerant solution is discharged inadvertently to ground or surface water. In normal operation, emissions will be within environmental discharge limits.

Emissions to land will be insignificant, except for spills from process accidents, or improper disposal of solid exchangers loaded with hazardous substances that would be leachable under the landfill conditions.

The above points address only the ion exchange process itself, and not disposal of spent or degraded ion exchange materials. These materials should be disposed of (after proper cleaning to remove the hazardous substances) with other solid industrial wastes of similar composition.

There are no special land use factors associated with ion exchange processes. Fixed-bed operations are run with the beds next to each other, with intermediate pumping. Continuous systems do require some overhead height for the loop, but have greatly decreased floor space requirements.

The only safety problems that might arise involve handling and processing the spent regenerant liquor with its potentially high concentrations of hazardous substances.

C. ECONOMIC ANALYSIS

Although ion exchange has been used extensively in treatment of wastewaters, it is frequently incorporated into systems with other treatment processes, such as reverse osmosis. In most cases, separate cost data are not available for ion exchange alone. There is also some reluctance on the part of many practitioners to divulge treatment cost data. Costs vary widely; stream size and composition are the primary determinants.

Some care should also be exercised in comparing different processes, since the end products are rarely the same. The ion exchange and liquid ion exchange costing examples in this study do not yield the same products and hence are not strictly comparable.

1. ADL Economic Analysis

As an example for cost estimating, a dilute mixed waste stream from a metal finishing operation was selected.

Feed Stream to Process: dilute mixed aqueous waste from metal finishing, 80,000 gallons/day (303m^3/day) containing:

zinc	15 mg/l
copper	0.5 mg/l
cyanide (total)	19 mg/l
chromium	22 mg/l [nearly all Cr(VI)]
pH	10 (approximately)

Treatment objective: to provide effluent which meets discharge requirements for zinc (<1 mg/l), copper, chromium and cyanide (all < 0.3 mg/l), pH 6-8.5; cyanide to be separated from metals.

Design Basis: 24 hour/day – 350 days/year
3 bed system, in duplicate for regeneration
24 hour loading time

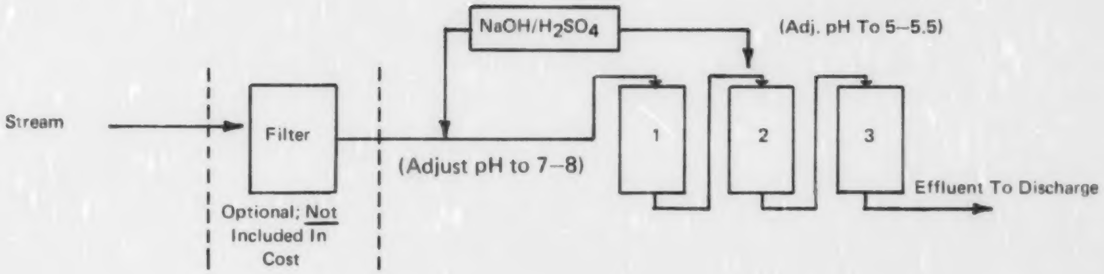
Product Streams: clean water; metal cations, chromium, cyanide.

Costs are listed in Table 2, and a schematic diagram is shown in Figure 2. The analysis indicates a treatment cost slightly in excess of $5/1000 gallons of influent. This is roughly comparable to the cost for liquid ion exchange – approximately $4/1000 gallons to treat the same stream. It should be noted, however, that the ion exchange process affords separation of the classes of hazardous species, while the liquid ion exchange costing example and many non-electrolytic membrane processes do not.

2. Process Economics

a. Operating Costs

Ion exchange is a reagent-intensive process. The chemical stoichiometry requires at least one chemical equivalent (molecular weight of species divided by its valence) be added for each one removed in the exchange. In practice, inefficiencies in operation often result in 1.5-2 equivalents being required per equivalent removed.


NaOH/H_2SO_4
(Adj. pH To 5–5.5)
Stream
Filter
1
2
3
(Adjust pH to 7–8)
Effluent To Discharge
Optional; Not Included In Cost

Column	Removes	Resin	Regenerant(s)	Effluent
1	Zn, Cu, Cr (III)	Chelating, Na^+ (Possibly Weak Acid)	H_2SO_4/NaOH	Metals In H_2SO_4
2	Cr (VI) (Possibly Some Metal Cyanides)	Weak Base, HSO_4^- Form	NaOH/H_2SO_4	$CrO_4^=$ In NaOH (Possibly Some Metal Cyanides)
3	CN^-	Strong Base, OH^- Form	NaOH	CN^- In NaOH

FIGURE 2 ION EXCHANGE PROCESS SEQUENCE

TABLE 2

ION EXCHANGE COST ESTIMATE

Variable Cost	Annual Quantity	Cost per Unit Quantity	Annual Cost
Operating Labor	2,200 MM	$12/hour	$26,400
Chemicals			
Resin Replacement (20%/yr)			2,800
– NaOH (70%)	175 tons	$60/ton	28,000
– H_2SO_4 (98%)	48 tons	$53.25/ton	2,600
Total Chemicals			$33,000
Utilities (Electricity)	75,000 kWh	$0.02/kWh	1,500
Maintenance (3% of Inv.)			12,000
Total Variable Costs			$73,300
Fixed Costs			
Taxes & Insurance (2% Inv.)*			$ 8,000
Capital Recovery (10 years @ 10%)*			64,700
Total Fixed Costs			$72,700
Unit Costs ($/$10^3$ gallons)			$5.21

*Estimated Capital Investment $400,000

Source: Arthur D. Little, Inc., estimates.

Resin replacement (generally 20-30 percent per year) is also a significant cost element; resin costs run $30-$180 per cubic foot with commonly used ones $40-$100.

Labor and maintenance costs are "normal" for chemical operations having typical equipment with pumps, valves, etc.

Energy requirements (steam, electricity) are low.

b. Capital Costs

Capital costs are relatively high. Materials must withstand service/regeneration requirements, and generally must be rubber lined or made of stainless steel. Systems vary in complexity. Instrumentation requirements are normal for wet chemical operations.

c. Product Credits

Some cost estimates take credits for product water and partial, or total, credit for reclaimable or recycled regeneration products. These should always be spelled out in detail so that the true unit cost of any ion exchange operation can be ascertained.

3. Comparison of Cost Estimates for Other Ion Exchange Processes

Cost estimates prepared for systems to remove chromium from cooling tower blowdown liquors have been given for a continuous countercurrent process (Ref. 46) (*Chemical Separations Corp.*) and for a fixed-bed process (Ref. 41) (*Rohm and Haas*) (Table 3). Since these estimates were prepared by experts in the respective areas, the estimates should have some basis in experience. Chemical costs shown in Table 3 were updated to sodium hydroxide at $160/ton and sulfuric acid at $53/ton.

TABLE 3

COST COMPARISON FOR CONTINUOUS AND FIXED BED SYSTEMS

Type	Continuous		Fixed Bed
Description	Cont. countercurrent mixed bed resins, removal and recycle of Cr (VI), removal of Cr (III) and Zn		3 bed "merry-go-round" weak base resin, removal and recycle of Cr(VI) only
Flow	700 gpm (1 million gpd)		1000 gpm (1.4 million gpd)
Cr (VI) content	20 mg/l		10 mg/l
Est. Capital Investment	$200,000 (approx. $20,000 resin)		$225,000 equipment $100,000 resin
Est. Operating Costs/Month	Chemicals:	$ 430	$820
	Resin:	350	820
	Labor:	$1,500	No labor or utility costs given
	Utilities:	150	

Source: (Ref. 46)

Some chemical cost savings will result with a continuous ion exchange system. However, since labor costs for the previous ADL example and the continuous system (Ref. 46) are between $1,500 and $2,000 per month, these particular ion exchange systems may not be representative for use of ion exchange in waste treatment, since the ion exchange process is frequently described by persons working in the chemical process field as having relatively low labor costs.

The above estimates put the treatment cost at less than $1/1000 gallons; however, these examples are extremely-high-volume applications. Recent operating costs for deionization of brackish water have put the cost of that operation at slightly more than $1/1000 gallons (Ref. 21).

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

A. BENEFITS AND LIMITATIONS

Pollution Potential	No air pollution – little potential for water pollution if hazardous species in regenerating solution are disposed of properly – little land pollution.
Classes of Waste	Will remove any dissolved salts from aqueous or partly aqueous solutions; solutions must be free of oxidants and suspended matter.
Breadth of Applicability	Can be used as primary treatment or clean-up after other primary treatment such as precipitation or reverse osmosis.
Operational Feasibility	Already demonstrated on many aqueous streams such as plating wastes, metal finishing wastes and waste streams from fertilizer production.
Economics	Treatment costs reasonable, around \$5/1000 gallons for separation of complex mixed wastes. Single bed polishing around \$1/1000 gallons. Credit for cleaned water suitable for re-use will help economics.
Energy	Little used in actual process.
Time Requirements for Development	Already in use.

B. MODIFICATIONS OR IMPROVEMENTS WHICH WOULD BE BENEFICIAL

The process equipment used in ion exchange is already well-developed. There are a variety of new exchangers now available, particularly the macroreticular types, which resist fouling and thus are more applicable to waste stream treatment. The apparent success in treating concentrated solutions such as steel pickling liquors should be followed up. Ion exchange could have application analogous to liquid ion exchange in separating components from liquors resulting from dissolution or leaching of waste solids.

C. RECOMMENDATIONS

- Since most of the usage and development activities for ion exchange in waste treatment are centered in the wastewater area, practitioners in that area, including exchanger manufacturers, IE systems designers and contractors performing government-sponsored research work should be consulted on a regular basis.

- Larger scale tests should be carried out on the ferrocyanide ion exchange method for removing cyanides from mixed streams, and on the use of chelating resins and other exchangers for the selective removal of heavy metals.

- Further research on the development and application of polymer beads impregnated with liquid ion exchange materials should be encouraged as a possible means for extending the concentration limits and selectivity of ion exchange.

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B. ORGANIZATIONS AND CONTACTS EXPERIENCED IN THE FIELD

1. Ion Exchange Materials — Manufacturers and Process Designers

- Rohm and Haas Co., Philadelphia, Pa.
  Dr. Robert Kunin, Mr. William H. Waitz, Mr. Gerald D. Button
- Dow Chemical Co., Midland, Michigan
- Diamond Shamrock Chemical Co., Cleveland Ohio and Morristown, N.J.

2. Ion Exchange Process and Systems Designers

- Chemical Separations Corp., Oak Ridge, Tenn.
  Mr. Irwin R. Higgins, Mr. Randhir C. Chopra
- Industrial Filter and Pump Co., Cicero, Ill.
  Mr. Charles Novotny
- Illinois Water Treatment Co., Rockford, Ill.
  Mr. Terry Dillman, Mr. James Moregard
- Dr. George Schorr, Westbury, N.Y.
- AJC Consulting Service, Columbia, Md.
  Mr. Angelo J. Casolo
- Mr. John Ciancia
  EPA Region II Laboratory, Edison, N.J.
- Oak Ridge National Laboratory, Oak Ridge, Tenn.
  Dr. K.H. Lin, Mr. L. J. King

3. Waste Treatment Users

- Singer Co., Elizabeth, N.J.
  Mr. Joseph DeVries (along with Dr. George Schorr)
- Almag Pollution Control Corp., Baltimore, Md.
  Mr. Frank Leach

LIQUID ION EXCHANGE

Prepared by

James R. Valentine

I. CONCLUSIONS AND RECOMMENDATIONS

Liquid ion exchange (LIE) can be used for selective removal and/or separation of free and complexed metal ions and other inorganic species from aqueous streams. It is competitive with conventional ion exchange, and can be used to treat much higher concentrations than the latter.

Present waste applications include removal of copper, nickel, zinc, molybdenum, chromium (VI) as well as nitric and hydrofluoric acids from various waste streams. Promising new processes include removal of cyanides from mixtures and recovery of metals from electroplating slimes.

Special economic incentives (tax credits for users, government-sponsored research) may be required for more rapid development of new applications and reagants, since historically such research has been stimulated principally by high volume hydrometallurgical applications.

The concept of employing high settler recycle rates for treatment of dilute streams should be subjected to further experimental testing.

II. PROCESS DESCRIPTION

A. BACKGROUND

Use of liquid/liquid extraction techniques for the separation of small amounts of free and complexed metals, especially for chemical analysis purposes, have been practiced since the 1800's. However, large-scale application of such processes for production of metals did not occur until the 1940's, when the requirements for high purity materials in the nuclear field encouraged rapid development of both new extraction reagents and process operations. Following declassification of atomic information in the 1950's, commercial exploitation in the hydrometallurgical processing of metals such as copper and nickel was rapid. However, the economics of the processes have generally limited their application to metals as costly as or more costly than copper.

B. UNDERLYING PRINCIPLE

The basic principle underlying the liquid ion exchange reactions* is the concept of distribution or partition between phases. When two immiscible phases are placed in contact, a substance that is soluble in both will be partitioned between those phases in a definite proportion. If the substance is much more soluble in one phase than the other, then the partition will favor the first phase. In the liquid ion exchange process, a water-soluble, ionic species is caused to become more soluble in an organic solvent (by salt formation, complexation etc.), thus promoting the partition or extraction of that species into the solvent.

C. OPERATING CHARACTERISTICS

1. Acceptable Feed Streams

Liquid ion exchange (LIE) involves the removal of ionic or undissociated inorganic species from an aqueous phase. Thus the process is applicable to any aqueous waste stream containing extractable species, and to any waste containing inorganic (particularly metallic) materials that can be dissolved in aqueous acid or alkali to yield an extractable species.

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*Note on Terminology: The term "liquid ion exchange" is being used to avoid confusion with the process of "solvent extraction of organics" which is the subject of a separate report. In many industrial processes, especially in hydrometallurgy, the term "solvent extraction" (or SX) is used more frequently than "liquid ion exchange" in describing these processes for separating and concentrating inorganic species in aqueous streams.

In the present context, "liquid ion exchange" includes all those processes that involve the removal of inorganic species from an aqueous solution via transfer to an immiscible solvent. Such processes include ion exchange, formation of complexes and chelates, and true solvent extraction.

For example, LIE can be used to remove the following inorganic species:

- Virtually all metallic elements (as soluble cations), although selectivity preferences of presently available extractants are generally for heavy polyvalent metals: common alkali metals are not easily extracted.
- Anions, including monatomic species such as halides, metal oxyanions such as chromate, and complexed metal species such as iron cyanides.
- Soluble but undissociated compounds such as mercuric chloride, and relatively weak acids such as hydrofluoric.

In theory, there is no upper limit to the concentrations of species in an aqueous stream that can be treated by this process; however, the relative volume of extractant employed would have to be so high that no usable phase separation would occur. Commercial processes for the extraction of nickel and cobalt treat solutions containing up to 10 g metal/liter (~0.2 mol/liter) (Refs. 2, 5, 13, 15); this is probably a typical concentration range, since extractants are generally employed in the 0.1 mol/liter range (Ref. 5).

Obviously the hazardous waste should contain no surfactant materials which would result in changes in separation behavior. In addition, strong oxidants are likely to result in some degradation of the functional groups on the extractants. The presence of much suspended solid matter (0.1%) may have a detrimental effect on the operation (Ref. 19).

2. Process Operation

LIE involves transfer of a species of interest from the aqueous phase into an immiscible organic phase, an operation generally termed "loading." The extracted aqueous phase is then termed the "raffinate." This "loaded" organic phase is, in turn, contacted with a second aqueous phase, whose composition is such that the species of interest will now transfer to this new aqueous phase. This second transfer process is termed "stripping," and the second aqueous phase is often referred to as the stripping liquor. In each case, the driving force for the interphase mass transfer is the formation of a more stable compound or a more highly-solvated (lower-energy) species. The process affords concentration of the species of interest at each phase change by selection of the appropriate ratio of phase volumes.

By use of appropriate chemical reagents in the two phases, selective removal (transfer) of one or another species from a phase is accomplished, thus affording separation of species present in the original solution. The species of interest may be extracted into the organic phase as an ion (complexed or solvated), an ion pair, or as an un-ionized compound, according to the oxidation state(s) of the element(s) involved, the nature of the complexing agents in either phase, and the pH (acidity) of the aqueous phase.

Stripping is frequently carried out with aqueous acid or base, and a "regeneration" of the organic phase may be necessary prior to the next loading, as, for example, when an amine-acid salt extractant is stripped with a base. Significant changes in extraction behavior can be brought about by relatively small changes in the above parameters, so that LIE may be applied to a wide variety of hazardous waste streams.

Because of the dependence on a constant distribution coefficient and on proper timing for phase separation, the LIE is essentially a steady-state process and should be run as a continuous (rather than batch) operation.

3. Output Streams

The process yields two aqueous streams, the raffinate or cleaned stream, and the loaded (or "pregnant") stripping liquor. The organic phase is virtually always run in a "closed loop." Both the raffinate and stripping liquor will contain small amounts (generally 5-50 mg/l) of the extraction solvent.

In the usual operations of solvent extraction, the aqueous regeneration stream used to strip the extracted species from organic solvent has a higher concentration of that species than did the original waste stream. In some processes, this regeneration stream is frequently brought to fairly high concentrations so that the components may be sent directly back to the process without further treatment; this is the case with stainless steel pickling acids (Ref. 3) and zinc from rayon processing (Ref. 3). If a direct recycle is not desired, then the concentrated regeneration stream can be treated by more conventional precipitation or electrolytic procedures (Refs. 2, 9).

In any case, the "loaded" organic phase, prior to regeneration, does *not* represent a suitable form for disposal or storage of the species of interest *unless* ultimate disposal or decomposition of the species by incineration is planned.

D. EQUIPMENT AND MATERIALS

1. Equipment

Since the extraction processes are "steady-state" phenomena which are reached only after a certain period of operation following start-up, virtually all commercial extraction operations are designed for continuous operations, for ease of operation, efficiency and economy. Liquid-liquid contacting processes should provide intimate mixing to maximize mass transfer (which is much slower than in a gas-liquid process) and should also provide a sufficiently long settling or quiescent period to allow the phases to separate. Three general classes of contactors are mixer-settlers, differential contactors, and centrifugal contactors.

Mixer-settlers are simplest in concept and design, but a single unit is rarely sufficient; the desired separation usually requires a series of units, with consequent multiplication of costs (Refs. 7, 8, 10, 13, 23, 24). For maximum efficiency, these stages are always run with countercurrent flows. Mixer-settlers are by far the most common extractors used in commercial recovery of nickel and copper from ores (Refs. 5, 13). Because of the large time constants and flow limitations of settlers in comparison to differential types, mixer-settler systems are least able to respond to changes in process conditions such as feed composition.

Differential contactors are run in a tower or column configuration, and the more efficient ones generally use some form of power input to promote mixing, rather than depending upon differences in the density of the phases in a spray or packed-tower mode (Refs. 7, 8, 23, 24). One widely used unit is the pulsed column, in which the phases are subjected to rapid, low-amplitude pressure pulses while flowing through perforated mixing plates (Refs. 7, 10). Other types of columns enhance mixing with rotating baffles or disks (Ref. 10).

Centrifugal contactors – a special type of differential contactor – have a very short contact time, but do provide excellent phase separation with virtually no entrainment (Refs. 7, 10, 23, 24). These are widely used in the nuclear processing industry to give clean separations while minimizing exposure of the extractant to conditions that may result in degradation. Centrifugal contactors also are able to respond very quickly to process condition changes, but they have necessarily complex and demanding control systems.

2. Reagents in Common Use for Liquid Ion Exchange

The principal types of extraction reagents which have been or are in common commercial use are listed below. The reagents are classified according to differences in the nature of the loading and stripping chemistry. In nearly all cases, these reagents are employed as dilute (5% to 30%) solutions in one (or a mixture) of the solvents and diluents listed below (i.e., inert solvents) in order to obtain an organic phase with the necessary low water solubility and handling (i.e., contacting and separating) properties. In some cases, one or more examples of commercial trade names are given.

a. Basic Extractants

These materials react with acids or metallic ions to form salts or complexes soluble in organic solvents. Some examples, in order of decreasing basicity, are:

- Amines, in particular long chain (C_{10}–C_{14}) secondary and tertiary amines (Alamines, Adogens): these are also frequently used in the acid salt form made by reacting with appropriate acid, and then function as ion exchangers.

- Trialkylphosphates, in particular the tributyl and trioctyl esters.

- Ketones, such as methylisobutylketone.

- Ethers, such as chloropropylether.

b. Acidic Extractants

These materials react with bases (neutralization) or with salts by exchange of cations. The materials may be employed as salts as well as free acids. Examples are:

- Mono- and dialkylesters of phosphoric acid, particularly the dioctyl ester.
- Carboxylic acids, particularly long chain and alicyclic (naphthenic) acids
- Naphthalene and alkylnaphthalene sulfonic acids

c. Chelating Extractants

These materials form stable chelate complexes with metal ions. They may exchange a hydrogen ion for the metal (thus having a pH dependence in the extraction chemistry) or they may carry a counter-ion along with the chelated metal. Examples are:

- alkyl substituted 8-hydroxyquinoline (Kelex 100)
- α and β-hydroxyoximes (LIX63N and LIX65N, SME529)
- β-diketones such as 2,4-pentanedione

d. Ionic Extractants

These materials are themselves ionic and form organic-extractable ion pairs either with anions or with cations. Examples are:

- tetraphenylborate anion, for extraction of cations
- long chain quaternary ammonium cations, for extraction of anions

e. Inert (non-complexing) Solvents

Inert (non-complexing) solvents of varying polarity will assist in the extraction. For example:

- kerosene type solvents are widely used as non-polar diluents for long chain amine extractants;
- aromatic solvents such as diethylbenzene are used frequently with aromatic reagents;
- chlorinated solvents, such as chloroform or chlorobenzene, which will solvate chelates and ion pairs more effectively than hydrocarbons;
- long chain alcohols, such as tridecyl alcohol, are frequently added to aid reagent solubility and phase separation.

III. APPLICATIONS TO DATE

A. PRINCIPAL CURRENT APPLICATIONS

The first industrial-scale uses of the process were in the preparation of nuclear reactor materials (zirconium, etc.), followed by more widespread usage in hydrometallurgy of copper, nickel, etc.. Today, LIE has widespread use in the hydrometallurgical processing of copper, nickel, cobalt, molybdenum and uranium, as well as significant uses in other nuclear materials processing (Refs. 5, 13, 16, 17, 21, 23). There is a large body of information on these fields, and it would be inappropriate to attempt to summarize in this report results in those fields, except where a point pertinent to waste processing may be made. A number of solvent extraction processes have been reported for the recovery of copper (Ref. 4) and nickel (Ref. 5) from ores, of copper from dump leach liquors (Ref. 2), of vanadium from various sources (Ref. 12) and of uranium from ores (Ref. 11).

There are also many applications of this technology to treatment of aqueous waste streams and streams resulting from total or selective dissolution of some solid wastes. Some of the commercial and near-commercial processes are listed below. In most cases, separate cost data for the liquid ion exchange process alone are not available. In some cases where competition may be keen, there is an understandable reluctance to release any economic figures.

1. Metal Pickling Liquors

In Sweden (Refs. 3, 6) liquors from pickling stainless steel are extracted with tributyl phosphate to recover nitric and hydrofluoric acids and molybdic acid. Iron, chromium, and nickel are recovered by precipitation. This process has been operating successfully for three years at a plant producing 70,000 tons of steel per year.

2. Zinc Recovery from Rayon Manufacturing Wastewater

Zinc from rayon manufacturing waters at a Swedish plant is recovered by solvent extraction with dioctyl phosphoric acid (Ref. 3). Pilot plant results indicated that the value of the zinc would pay off the plant investment in 6-7 years. A plant to treat 900 gallons/minute of 0.04% zinc solution was due on-stream in 1975.

3. Copper Recovery from Scrap and Etchant Solutions

Copper has been recovered from spent alkaline etchant solutions from electronics manufacturing processes (Refs. 13, 18) and from ammonia/ammonium carbonate leaching of metallic copper scrap (Refs. 13, 14) via extraction (as amine complexes) with commercial copper extracting reagents.

4. Small-Scale Hydrometallurgical Processes

Most operating experience with LIE for hydrometallurgical processing has been gained on very large-scale (many tons/day) systems. However, one system for recovering relatively small amounts of nickel (0.5 ton/day) and copper (up to 1 ton/day) from an aqueous waste stream from prior copper processing applications by means of extraction and electrowinning has run economically (Ref. 14). The feed stream generally contains less than 1% (W/V nickel and even less copper.

C. POTENTIAL APPLICATIONS TO WASTE TREATMENT

Many possible LIE applications in waste treatment are at least at the pilot or laboratory stage; some may have been tested further, but results have not been published. Hughes has recently published a summary of the status of some of these processes (Ref. 15).

Iron, zinc, copper, nickel and chromium are reported to be recoverable from alkali hydroxide sludges (*not* liming sludges) by the MAR process (Ref. 3). The sludge solids, which were reported to contain a very high percentage (95%) of recoverable metals, are dissolved in acid and subjected to three sequential extraction steps. The first extraction, with LIX64N (hydroxyoxime), removes copper; the second with di-2-ethylhexyl-phosphoric acid, removes both iron and zinc, which are subsequently separated by stripping with dilute sulfuric acid to remove zinc and more concentrated acid to remove iron; the third is with MX-200 (a proprietary solvent from MX-Processor AB), which removes nickel but not chromium. The metals are recovered by precipitation as hydroxides or salts. A demonstration scale (500 ton/year) plant is under consideration.

Zinc, copper, nickel and chromium can be recovered from slags and ashes by a three-step extraction process analogous to the MAR process, except that an oxidizing leach with nitric acid is used to extract the metals (Ref. 3). The nitric acid is recycled to minimize losses.

An extraction process for removing cyanide and zinc from electroplating rinsewaters has been tested extensively in a laboratory-scale liquid ion exchange circuit (Refs. 17, 20, 21). The process uses a quaternary amine reagent plus tridecyl alcohol and a kerosine carrier in a two-stage-extractor/two-stage-stripper unit. Stripping is accomplished with 6 molar sodium hydroxide. Cyanide was decreased from 40 mg/l to 0.4 mg/l and zinc from 23 mg/l to 0.7 mg/l. Chemical costs were predicted to be less than $1/1000 gallons. The ratio of feed flow to stripping liquor flow was very high (65%). In order to maintain a usable feed/solvent ratio (2/1-4/1) in the contactor, a high recycle rate was maintained in the minor phase in each mixer-settler (Ref. 7).

Initial laboratory tests indicated the feasibility of an extraction process for removing traces of mercuric chloride from brines using a tertiary amine. Mercury could be reduced from 10 mg/l to the 0.001 mg/l level (Ref. 7). The concept of using a high internal recycle rate for the minor phase of each mixer-settler was advanced to allow a reasonable phase ratio.

Laboratory-scale tests of an extraction process for removing up to 100 mg/l of chromium (VI) from electroplating rinsewaters was successful (Ref. 22). Chromium levels could be lowered to less than 1 mg/l by two-stage extraction employing a quaternary or tertiary amine reagent. The quaternary amine gave quantitative extraction with solution pH's up to at least 8; the tertiary amine required pH2 or lower. The stripping solution was sodium hydroxide. The tests also indicated that storage in the loaded form resulted in degradation of the tertiary amine extractants.

A number of processes have been proposed and tested for recovery of nickel, cobalt, chromium and iron from the wastes from manufacturing and use of high-strength alloys (Refs. 2, 3). Processes have been developed by the U.S. Bureau of Mines, Gullspang Electrochemical Company (Sweden), and Metallurgic Hoboken (Belgium), among others, and employ a variety of extraction and metal recovery modes to cover many different alloy compositions (Ref. 2).

Spent catalysts and cinders have been treated for removal of zinc, cobalt, and nickel (Ref. 2).

Nickel and copper have been recovered from "dragout" rinses in nickel and copper plating lines (Ref. 9). In these tests considerable attention is given to the project costs as a function of quality of recycled materials and reagent losses.

Direct contact dissolution of metals in solid wastes using appropriate extractants (probably acidic) such as has been suggested for processing uranium ore (Ref. 11), may prove useful if recovery of the solvent from the solids is not difficult. This would be particularly advantageous for treatment of slags and residues from fossil fuel combustion, since use of an aqueous acid treatment to remove hazardous species such as heavy metals from the solids would also cause major amounts of alkali and alkaline earth compounds to be dissolved. These latter materials would not be removed by the liquid ion exchange treatment and consequently would remain in the aqueous effluent possibly necessitating further treatment of the effluent prior to discharge or reuse.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

The energy requirements for the solvent extraction process are low, consisting primarily of electricity for pumping and mixing; the driving force for the process is chemical.

B. ENVIRONMENTAL IMPACTS

Since solvent extraction is a solution process, emissions to the air will be negligible, except for possible volatilization of small amounts of extraction solvents or untreated raffinate (process stream after extraction).

The raffinate from the extraction generally will contain from 5 to 50 mg/l of the organic phase which may contain organic amines, phosphorus compound, aromatics, etc. This aqueous stream will have to be treated by absorption or secondary solvent extraction prior to discharge. This will not be a problem for closed cycle systems that both treat and yield solids.

The "regeneration" solution into which the hazardous components are stripped from the extraction solvent will contain those components at high concentrations. This solution must be treated to recover or to render the components innocuous without suffering leakage losses of solution.

No significant land disposal problems are anticipated.

The above points address only the extraction process, and not the disposal of degraded extraction solvents. Presumably these materials (obviously stripped of any hazardous materials which they might contain) can be disposed of with other solvent wastes of similar composition.

There are no special land-use factors associated with LIE processes. Mixer-settler operations can be run cascaded or pumped, so no great height is needed.

The only safety problem that might arise involves handling or processing the spent stripping liquor, with its potentially high concentrations of hazardous substance(s).

C. ECONOMIC ANALYSIS

A dilute mixed-waste stream from metal finishing operations was selected as an example for cost estimates. This stream is essentially identical to the one used for economic analysis of conventional ion exchange, thus allowing some comparisons between the two processes.

1. ADL Economic Analysis

Feed Stream to Process: dilute mixed aqueous waste from metal finishing. 80,000 gallons/day (303 m^3/day), containing:

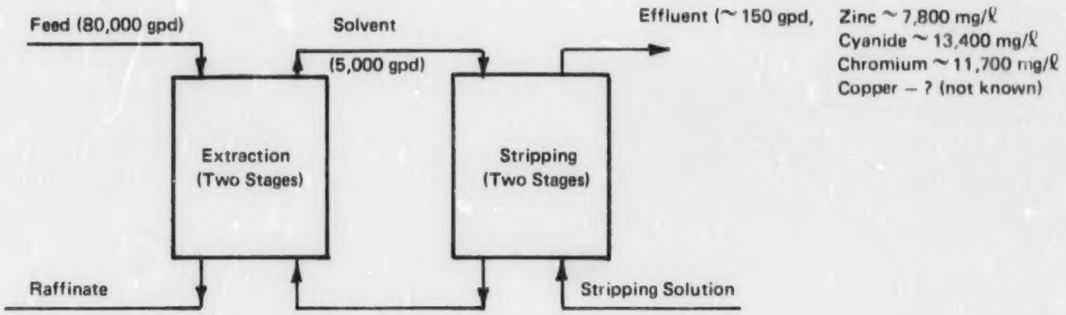
zinc	15 mg/l
copper	0.5 mg/l
cyanide (total)	25 mg/l
chromium	22 mg/l [nearly all as Cr(VI)]
pH	10 (approximately)

Treatment Objective: to provide effluent that meets discharge requirements of less than 1 mg/l for hazardous metals and inorganics; effluent may require further treatment to remove organics.

Design Basis: 24 hour/day, 330 days/year. Two stage mixer-settlers for extraction and stripping with high recycle rate for minor phase (0.25 minute mixing, 5 minutes disengagement times).

Extraction Solvent: 2.5% aliquot 336 + 20% tridecyl alcohol in kerosine.

Stripping Solution: 6 molar (24%) sodium hydroxide.


Feed (80,000 gpd)
Solvent
(5,000 gpd)
Effluent (~ 150 gpd,
Zinc ~ 7,800 mg/ℓ
Cyanide ~ 13,400 mg/ℓ
Chromium ~ 11,700 mg/ℓ
Copper – ? (not known)
Extraction (Two Stages)
Stripping (Two Stages)
Raffinate
Stripping Solution

In dilute operation, LIE is both chemical- and labor-intensive (see Table 1). If the same system were used to treat more concentrated solutions, then the chemical usage would be expected to increase proportionately. However, equipment and labor should not increase very rapidly since much higher concentrations could be handled by increasing the solvent and stripping liquor flows and decreasing the internal recycle rate.

TABLE 1

OPERATING COST ESTIMATES FOR LIQUID ION EXCHANGE

	Annual Quantity	Unit Quantity	Annual Cost
Variable Costs			
Operating Labor	2,200/hr	$12.00/hr	$ 26,400
Electricity	80,000/kWh	0.02/kWh	1,600
Chemicals			
Kerosene	330/gal	0.45/gal	150
Tridecyl Alcohol	700/lbs	0.37/lb	260
Aliquot	90/lbs	1.40/lb	130
Caustic (70%)	70/tons	180.00/ton	12,600
Total Chemicals			$ 13,140
Maintenance (4% Inv.)			12,000
Total Variable Costs			$ 53,140
Fixed Costs			
Taxes and Insurance* (2%/yr)			$ 6,000
Capital Recovery* (10%-10 yrs)			48,860
Total Fixed Costs			$108,000
Unit Costs ($\$/10^3$ gal)			$ 4.09

*Estimated capital investment: $300,000.

Source: Arthur D. Little, Inc., estimates.

2. Other Costs Estimates for Dilute Stream Treatment

Few economic studies have been made on treatment of dilute streams. Although somewhat out of date now, one estimate made in 1971 for LIE treatment of 7,200 gallons/day of a solution containing 100 mg/l of chromium (VI) indicated a cost of approximately $1.50/1000 gallons; however, the capital equipment costs in that study were extremely low, less than $10,000 (Ref. 22), so that the overall estimate appeared to be quite low.

The cost estimate developed above can be compared to the similar estimate for treating an essentially identical feed stream using conventional ion exchange. For ion exchange, the total estimated cost was $5.21/1000 gallons. However, one important difference between the processes is that the LIE raffinate will probably require further treatment to remove organics while the effluent from conventional ion exchange needs no further processing for re-use or discharge.

3. Economic Analyses for Treatment and Recovery of More Concentrated Streams

The investment and operating costs for the liquid ion exchange unit operation alone (divorced from pretreatment and materials recovery costs) are somewhat difficult to obtain from reports. However, at a 1967 conference industry experts agreed on a cost range of $100-$300 per ton of metal for a single extraction (5-stage) plant with backwash (Ref. 12). This range includes capital investment and operating costs including loss of extraction solvent. This range held for a variety of processes and metal concentrations.

Some more recent cost data for piloted processes are given in Table 2. In all cases the costs include the cost of subsequent recovery operations such as precipitation as oxide or hydroxides, or electrowinning.

From the above cost data, it is obvious why only relatively expensive metals (copper, etc.) have been investigated. Most cost data indicate that the value of the recovered metals exceed the operating costs. In addition, since liquid ion exchange can be designed to afford separation as well as concentration of various metals, the recovered product can be of very high purity.

TABLE 2

RECENT COST DATA FOR PILOTED PROCESSES

Process	Metal Recovery/Yr	Capital Costs ($)	Annual Operating Costs ($)	Total Unit Costs ($/ton metal)
Recovery of metals and acids from stainless steel pickling (Sweden) (Ref. 6)	Ni, Cr = 400 tons Fe = 400 tons	600,000	130,000	200-400 for all metals
Recovery of nickel and copper from low grade ores (USA) (Ref. 5)	25,000 tons	amortization and operating costs =		$140 for Ni $170 for Cu
Recovery of nickel from plating bath dragout (rinses) (UK) (Ref. 9)	7.2 tons	27,200	18,500	$3,000
Uranium from ore (Canada) (Ref. 12)	1,000 tons	amortization and operating costs =		$800 (clarified liquor) $400 (extraction of pulp)

V. OUTLOOK FOR LIQUID ION EXCHANGE IN INDUSTRIAL WASTE TREATMENT

A. BENEFITS AND LIMITATIONS

Pollution Potential	No air pollution – some potential for water pollution unless reclaimed extractants are stripped from discharge stream – little land pollution.
Classes of Waste	Will remove most dissolved ionic or un-ionized inorganics from aqueous streams, including metallic solid wastes; solutions should be free from surfactants and oxidants
Breadth of Applicability	Can be uses as a primary treatment or clean-up after other primary treatment such as precipitation
Operational Feasibility	Already demonstrated on various aqueous streams and wastes such as plating rinses, metal pickling liquors, and solid metal wastes
Economics	Treatment of dilute streams reasonable ($4/1000 gal). Present recovery processes on concentrated streams somewhat expensive ($200-$3000/ton of metal recovered) but value of recovered metal generally offsets this cost.
Energy	Little used in actual process – just pumping and mixing solutions
Time Requirements for Development	Already in use

B. MODIFICATIONS OR IMPROVEMENTS THAT WOULD BE BENEFICIAL

Process equipment in general is already at a high state of development. There are also great numbers and varieties of extraction reagents available, and presumably an even larger number in various stages of development at the companies which supply them. The key item now is the (economic) incentive to bring these developed tools to bear on waste treatment.

C. RECOMMENDATIONS

Some form of special economic incentive is needed since the development of new applications in this area has been centered traditionally around high volume markets. Government-sponsored applications projects is one method. Since much of the process development work in this area has been done by the extractant producers, they would be expected and should be encouraged to participate in such research.

The concept of employing mixer-settlers with high recycle rates for treating dilute streams should be tested at the pilot stage.

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B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD

1. Liquid Ion Exchange Materials – Manufacturers and Process Designers

   - General Mills Chemicals, Inc., Tuscon, Arizona; also Minneapolis, Minn., R. Brantley Sudderth

   - Shell Chemical Co., Houston, Texas

   - Ashland Chemical Co., Columbus, Ohio

- Rohm and Haas Company, Philadelphia, Pa., Mr. Gerald R. Button

2. Liquid Ion Exchange Process and Systems Designers

   - Oak Ridge National Laboratory, Oak Ridge, Tenn., Dr. William S. Groenier, Dr. Fletcher L. Moore.
   - Warren Spring Laboratory, Stevenage, England, Dr. Douglas S. Flett, Dr. Archibald W. Fletcher
   - Battelle Columbus Laboratories, Columbus, Ohio, Dr. Robert S. Cherry, Jr., Dr. G. Raymond Smithson
   - MX Processor AB, Mölndal, Sweden, Dr. Hans Reinhardt

3. Waste Treatment Users

   - Silresim Chemical Company, Lowell, Mass., Dr. John G. Miserlis
   - SEC Corporation, El Paso, Texas, Mr. James Cibella

LIQUID-LIQUID EXTRACTION OF ORGANICS

Prepared by

Warren J. Lyman

I. CONCLUSIONS AND RECOMMENDATIONS

Liquid-liquid extraction should be considered as a viable waste treatment process for selected, concentrated, and segregated waste streams primarily where material recovery is possible and desirable. Organic solutes may be recovered from both aqueous and organic solutions, in some cases at a net profit. The process usually requires the use of other unit processes such as distillation or stripping to effect solvent recovery (from the treated effluent) and solute recovery (from the solvent). These processes may account for the major portion of the costs and energy requirements of a total recovery system based on liquid-liquid extraction.

Present applications are concentrated in two areas: (1) the recovery of phenol from aqueous wastes, and (2) the recovery of halogenated hydrocarbon solvents from organic solutions containing other water-soluble components. Extraction in the former case is with an organic solvent and in the latter case with water (to remove the water-soluble component).

Potential applications will generally be similar situations. For example, aqueous wastes containing one, or just a few, valuable organic solutes in concentrations of a few hundred ppm to a few percent may be economically treated. Competing processes will include adsorption (in the lower concentration ranges) and stripping (for the more volatile solutes). Organic solutions containing a mixture of water-soluble and non-water-soluble components may be economically treated by extraction with water. Here stripping or distillation will be competitors when the vapor pressures of the two components are far enough apart.

Costs of processes involving extraction will vary widely and will, in general, be least when an efficient system can be designed to treat a concentrated waste stream in such a way that one, or just a few, (theoretical) extraction stages are required.

The development and final design of a specific liquid-liquid extraction processing unit for a new application should be preceded by detailed laboratory tests and a technical and cost comparison with competing processes. Aqueous waste treatment applications especially will involve the consideration of several parameters, thus compromises will usually be necessary. Each new situation must be studied on a case-by-case basis, and there are few assurances that extraction will be found practical or economical except in the limited domains outlined above.

II. PROCESS DESCRIPTION

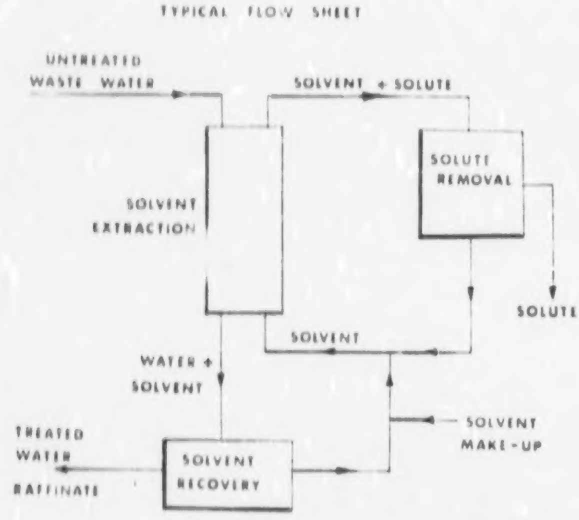
A. BACKGROUND

Liquid-liquid solvent extraction, hereinafter referred to just as solvent extraction, is the separation of the constituents of a liquid solution by contact with another immiscible liquid. If the substances comprising the original solution distribute themselves differently between the two liquid phases, a certain degree of separation will result and this may be enhanced by use of multiple contacts.

This process description deals only with the extraction of relatively un-ionized species where the primary forces of attraction between the solute and the solvent are not ionic. A separate report, entitled "Liquid Ion Exchange" has been prepared to cover the special case of ionized substances. Solvent extraction, as described in this report, is generally applicable to the removal of certain organic chemicals, primarily from water or, much less commonly, from other solvents.

B. UNDERLYING PRINCIPLES

The solvent extraction process is shown schematically in Figure 1. This diagram shows a single solvent extraction unit operating on an aqueous stream; in practice this unit might consist of (1) a single-stage mixing and settling unit, (2) several mixers and settlers (single-stage units) in series, or (3) a multi-stage unit operating by countercurrent flows in one device (e.g., a column or differential centrifuge).


TYPICAL FLOW SHEET
UNTREATED WASTE WATER
SOLVENT + SOLUTE
SOLUTE REMOVAL
SOLVENT EXTRACTION
SOLUTE
SOLVENT
WATER + SOLVENT
SOLVENT MAKE-UP
TREATED WATER
RAFFINATE
SOLVENT RECOVERY

Source: Ref. 1.

FIGURE 1 SCHEMATIC DIAGRAM OF SOLVENT EXTRACTION OF WASTEWATER

As Figure 1 indicates reuse of the extracting solvent (following solute removal) and recovery of that portion of the extracting solvent that dissolves in the extracted phase are usually necessary aspects of the solvent extraction process. Solvent reuse is necessary for economic reasons; the cost of the solvent is generally too high to consider disposal after use. Only in a very few cases may solvent reuse be eliminated; these cases arise where an industrial chemical feed stream can be used as the solvent and then sent on for normal processing, or where water is the solvent. Solvent recovery from extracted water may be eliminated in cases (1) where the concentration in the water to be discharged is not harmful, and (2) where the solvent loss does not incur a high cost.

The end result of solvent extraction is to separate the original solution into two streams, (1) a treated stream (the raffinate), and (2) a recovered solute stream (which may contain small amounts of water and solvent). Solvent extraction may thus be considered a recovery process since the solute chemicals are generally recovered for reuse, resale, or further treatment and disposal.

C. OPERATING CHARACTERISTICS

1. Waste Forms That Can Be Treated

Solvent extraction will work only on liquid solutions, though some degree of emulsification and suspended solids may be tolerated. Solvent extraction is theoretically applicable for the removal of almost any solute from any liquid solution. In practice, it is probably much more limited and is best suited, with current technology, for the removal of organic solutes from aqueous solutions and for the removal of water soluble components in organic solutions.

Although solvent extraction is usually considered for the extraction of a single chemical species (or perhaps a few chemically similar species), there is no necessity for such a limitation. A mixture of quite different chemical species (solutes) in a solution may be extracted at the same time; the efficiency of extraction may vary greatly, however, for different chemicals. It should be noted that some of the EPA funded contracts identified in Section III below are investigating problems of this nature.

Solvent extraction can theoretically be used for any solute concentration, though there may be restrictions at times, depending on the specific solute and solvent involved. For example, when the solute and solvent are miscible with each other in all proportions, there exists an upper limit in solute concentration (in the feed) above which it is not possible to extract any solute with that solvent. Extraction may be easier, in a practical sense, at low solute concentrations as (1) lower solvent-to-feed ratios could probably be used and (2) a solvent with very low solubility in the raffinate could be used thus eliminating the need for solvent recovery from the raffinate. On the other hand, low concentration aqueous solutions are likely to be more economically treated either by adsorption (e.g., with carbon or resins) or by stripping.

Moderate to high concentration solutions are somewhat more difficult to treat then low concentration solutions but are more likely to be economically treatable by solvent extraction. Applications of solvent extraction exist where the solute concentration in an aqueous solution is several percent (by weight); examples include phenol and acetic acid removal with concentrations up to about 5%. The concentration factor is not so restrictive when organic solutions are being extracted; in one typical case (see the first example in Section III-A26) the concentration of the extracted component is typically around 15% and may be as high as 60% or 70%. For aqueous solutions, if a solute is present in concentrations higher than about 10%, it is likely that solvent extraction, while still possible, may become impractical. This could be true, for example, if the solute has a strong hydrophylic nature and would thus require the use of a solvent that also was somewhat hydrophylic in order to obtain a respectable extraction efficiency. The use of such a solvent would probably lead to problems with solvent recovery from the raffinate.

Limitations on suspended solids will depend primarily on the type of extracting equipment used.

2. Chemical Classes That May Be Treated in Aqueous Waste Treatment

The discussion below considers only the extraction of organic solutes from aqueous solution with organic solvents as (1) this is a likely case to be encountered and (2) there is only very limited information on other systems.

As implied in subsection 1 above, it is generally possible to find a solvent that will extract almost any given organic solute from water. In general, the less water-soluble a solute is, the easier it will be to extract. In addition to the use of actual solubility data as a guide, three rules of thumb may be used:

(1) For a given carbon skeleton, the more hydrophylic the substituents are, the less extractable the substance will be. See, for example, the listing in Table 1.

(2) The hydrophylic nature of various substituents is roughly additive. Thus, information such as is given in Table 1 may be used to estimate the relative hydrophylic nature of different chemicals with two or more substituent groups.

(3) Increasing the number of carbon atoms in any homologous series of chemicals will decrease the hydrophylic nature and thus improve extraction.

The above are only general guides, and the importance of a detailed case-by-case evaluation cannot be overemphasized. This is due to the fact that there are numerous other important parameters to consider in assessing the potential for solvent extraction. Chief amongst these other considerations are (1) the choice of solvent, and (2) the determination of the optimum solvent-to-solution ratio (and associated flow rates).

TABLE 1

CHANGES IN PARTITION COEFFICIENT* WITH CHANGES IN CHEMICAL SUBSTITUENTS AND STRUCTURE

Key: R = Organic molecule
X = Substituent group or structure change on R
P = Partition coefficient for chemical between an organic solvent and water (at low solute concentrations).

X	Aliphatic R $\log P_{RX} - \log P_{RH}$	Aromatic R $\log P_{C_6H_5X} - \log P_{C_6H_6}$
– OC_6H_5	1.61	2.08
– I	1.00	1.12
Intramolecular H-bonding	.65	–
– Br	.60	.86
– CH_2	.50	.50
– SCH_3	.45	.61
– Cl	.39	.71
Ring Closure	-.09	–
– F	-.17	.14
Branching in C chain	-.20	–
Branching of functional group	-.20	–
– $COOCH_3$	-.27	-.01
– $N(CH_3)_2$	-.30	.18
Double Bond	-.30	–
– OCH_3	-.47	-.02
Folding	-.60	–
– COOH	-.67	-.28
– $COCH_3$	-.71	-.55
– CN	-.84	-.57
– NO_2	-.85	-.28
– O –	-.98	–
– OH	-1.16	-.67
– NH_2	-1.19	-1.23
–C=O	-1.21	–
– $CONH_2$	-1.71	-1.49

*A partition coefficient is the ratio of concentrations of a chemical in two immiscible liquid phases at equilibrium.

Source: Leo, A., Hansch, C., and Elkins, D., "Partition Coeffients and Their Uses," *Chemical Reviews, 71* (6), 525-616 (1971)

With respect to solvent choice, economic and practical considerations clearly demonstrate that the solvent should have (1) a high distribution coefficient for the solute (i.e., high extracting power), (2) a low solubility in water (to reduce losses), and (3) a low cost. Other solvent considerations relate to selectivity (Preference for extracting the solute rather than water), recoverability, density and interfacial tension (for good phase separation), chemical reactivity, viscosity, vapor pressure, freezing point, and hazards. (See Ref. 2 for additional information on this subject.)

3. How Process Operates

A process for solvent extracting a solution will typically include three basic steps (see Figure 1): (1) the actual extraction, (2) solute removal from the extracting solvent, and (3) solvent recovery from the raffinate (treated stream). The process may be operated continuously.

The first step, extraction, brings the two liquid phases (feed and solvent) into intimate contact to allow solute transfer either by forced mixing or by countercurrent flow caused by density differences. The extractor will also have provisions to allow separation of the two phases after mixing.

One output stream from the extractor is the solute laden solvent; some water may also be present. Solute removal may be via a second solvent extraction step, distillation, or some other process. For example, a second extraction, with caustic, is sometimes used to extract phenol from light oil which is used as the primary solvent in dephenolizing coke plant wastewaters. Distillation will usually be more common, except where problems with azeotropes are present. In certain cases, it may be possible to use the solute-laden solvent as a feed stream in some industrial process, thus eliminating solute recovery. This is apparently the case at some refineries where crude or light oil can be used as a solvent (for phenol removal from water) and later processed with the solute in it. Other similar applications probably exist and are particularly attractive since they eliminate one costly step.

Solvent recovery from the treated stream may be required if solvent losses would otherwise (1) add significantly to the cost of the process, or (2) cause a problem with the discharge of the raffinate. Solvent recovery may be accomplished by stripping, distillation, adsorption, or other suitable process.

4. Output Streams

In general, solvent extraction separates the original contaminated stream into two streams: (1) a purified stream (e.g., purified water) and (2) assuming solvent recycle, a relatively pure solute stream. This solute stream is thus the main process emission; but since the solute is recovered, recycle or resale of this "emission" will generally be possible.

Lesser emissions will include the following:

- Residual (low-level) amounts of the contaminant in the purified waste stream;
- Small solvent losses in the purified waste stream;
- Fugitive emissions of the solvent into the air;
- Heat (e.g., from solute removal or solvent recovery if distillation or steam stripping is used);
- Small solvent losses in the recovered contaminant.

C. EQUIPMENT AND MATERIALS

There are several different types of contractors available for solvent extraction; some of the major differences between them are described below. The reader should refer to other sections of this manual for descriptions of other pieces of equipment, e.g., stills, that are often part of a solvent extraction process.

There are two major categories of equipment for liquid extraction:

(1) Single-stage equipment where the fluids are mixed, extraction occurs, and the insoluble liquids are settled and separated. A cascade of such stages may then be arranged. A single stage must provide facilities for mixing the insoluble liquids and for settling and decanting the emulsion or dispersion which results. In batch operation, mixing together with settling and decanting may take place in the same or in separate vessels. In continuous operation, different vessels are required.

(2) Multi-stage equipment, where the equivalent of many stages may be incorporated into a single device or apparatus. Countercurrent flow is produced by virtue of the difference in densities of the liquids, and with few exceptions the equipment takes the form of a vertical tower which may or may not contain internal devices to influence the flow pattern. Other forms include centrifuges, rotating discs, and rotating buckets. Depending upon the nature of the internal structure, the equipment may be of the stagewise or continuous-contact type.

Examples of various types of contactors are given in Table 2.

TABLE 2

CLASSIFICATION OF CONTACTING EQUIPMENT

Type of Agitation	Discrete Stage Contact	Continuous Contact
None		Spray column Baffle plate column Packed column Sieve-tray column
Rotary devices	Holley-Mott Simple mixer-settler Pump-mix mixer-settler Individual stage centrifuges Stacked-stage mixer settler	Scheibel column Oldshue-Rushton column Rotating disc contactor Multistage mixer column Podbielniak extractor Alfa Laval extractor Luwesta
Pulsed	Pulsed mixer-settler	Pulsed packed column Pulsed sieve-plate column

Source: Ref. 3

The choice of one particular contractor involves the consideration of several factors. Some of these are discussed by Logsdail and Lowes (Ref. 3) as follows:

Number of Stages Required – All types of extractor can be used satisfactorily when few, say two or three, theoretical stages are required. When more than this, perhaps ten or twenty, are needed, then the choice becomes limited: spray towers, for instance, would be 100 feet or more in height. For processes requiring more than twenty stages, a series of mixer-settlers or several columns in series would probably have to be used.

Capacity – For low and moderate throughputs, a spray or packed column could be used; for intermediate and high throughputs, a rotating disc-contactor, pulsed plate column, or mixer-settler could be used. Of these, a pulsed plate column probably has the highest throughput per unit volume of contactor, except for the centrifugal types.

Solvent Residence Time – Some processes may demand that the solvent residence time be short to minimize solvent degradation and holdup. A contactor having assisted settling such as one of the centrifugal types would be preferable for this purpose. Gravity settling mixer-settlers require long residence times, particularly if several stages are required, since settling and phase separation must occur at each stage and will depend on the rate of coalescence of the dispersed phase. In the differential contactors, settling and phase separation occurs only at each end; thus the residence time is solely a function of the mean droplet rising (or falling) velocity and does not involve the coalescence rate.

Phase Flow-Ratio – In all continuous differential contacts in which the dispersed phase hold-up is a fraction of the phase flow-ratio, the performance decreases as the ratio of the dispersed to continuous flow-rate decreases.

Physical Properties – The drop size in differential extractors is a function of the parameter $(\sigma/\Delta\rho)$, where σ is the interfacial tension and $\Delta\rho$ the density difference between phases; thus, large values of this parameter correspond to large drops and hence to a low interfacial area which is commensurate with poor mass transfer performance. With mechanically agitated contactors the drawbacks of a system having a high interfacial tension, and hence high $(\sigma/\Delta\rho)$ value, can be overcome by increasing the power input to the system. Thus, a certain degree of flexibility is available for matching the mass transfer efficiency and capacity to give the required performance. When phases having high viscosities are used, a mechanically agitated extractor will generally have better performance than a non-agitated one of the same size.

Direction of Mass Transfer – For aqueous solvent systems, the drop size generally increases when mass transfer occurs from the solvent to the aqueous phase. This may lead to a poor performance of spray and packed columns but can be overcome in mechanically agitated contactors by increasing the power input. Little information is available for non-aqueous systems and the effect of the direction of mass transfer would have to be obtained from experimental data for each system.

Phase Dispersion and Hold-up – To obtain the greatest interfacial area over which mass transfer can be effected, the phase having the highest throughput should be dispersed. Some difficulty may be encountered, however, if it is desired to disperse the aqueous phase in column contactors since many packings and constructional materials are preferentially wetted by an aqueous phase. If this happens, the dispersed phase will move through the column in streams, films and large irregularly shaped drops, rather than as discrete drops, giving rise to a poor performance. Hydrophobic materials are available and can be used so long as they withstand the service conditions. If contamination of the extract phase is likely to occur due to the collection of particular impurities at the interface in a column contractor, then the phase dispersion should be such that the interface is at the raffinate end of the column. If a low hold-up of one of the phases is desired, for instance when handling unstable solutes or high-cost solvents, minimum contact time and contactor volume are required. These requirements are best met with one of the centrifugal contactors.

Slow Reactions – When a slow reaction is involved, either at the phase interface or in one of the phases, then a long residence time per stage may be required. Long residence time can best be obtained by having some control over the rate of recirculation within each stage. Mixer-settlers serve this purpose.

Presence of Solids – When solids are present in one or both of the feeds, many types of extractor would have to be shut down periodically to remove solid deposits. An exception is the pulsed plate column, which to a large extent is self-cleaning, and the Luwesta centrifugal extractor, which has provisions for solids removal. It is also claimed that the Graesser contactor can handle solids in suspension.

Overall Performance – A knowledge of overall contactor efficiency is valuable in fixing column dimensions and operating conditions for a particular process. In order to assess the performance of an extractor it is useful to combine the throughput and mass transfer efficiencies in a single figure of merit. For continuous differential extractors, this can be done by means of a performance index, defined as the ratio of the mass of the superficial phase flow rates at flooding to the HTU.* This index is a modified transfer coefficient and provides a combined measure of the solute transfer efficiency and capacity per unit volume of column. A comparable index for stagewise contactors is the ratio of the sum of the volumetric phase flow rates at flooding divided by the total volume of one stage. The index can be used for comparing different extractors with each other, the higher the index the better the performance, so long as identical feed solutions are used. Such comparisons should be made on the same system. Unfortunately, adequate published data are not available for this purpose.

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*HTU-overall height of a transfer unit.

III. APPLICATIONS TO DATE

A. PRINCIPAL CURRENT APPLICATIONS

At present, solvent extraction is in limited use in both commercial processing and in waste treatment applications. Included are the following:

1. Commercial Process Applications (Refs. 1,4)

a) Manufacture of lubricating oil from crude oil; saturated paraffins are extracted in a dewaxing operation with such solvents as phenol, furfural, propane, nitrobenzene, benzene, and cresylic acids.

b) Upgrading of gasoline, which involves the separation of aromatics from low-octane paraffins; diethylene glycol may be used as the solvent.

c) Extraction of sulfur compounds from gasoline; the solvent can be an aqueous sodium hydroxide solution, a methanol-water mixture, or others.

d) Recovery of valuable products (from waste streams) and purification of recycle solvents in the plastics industry.

e) Refining of vegetable oils and fats.

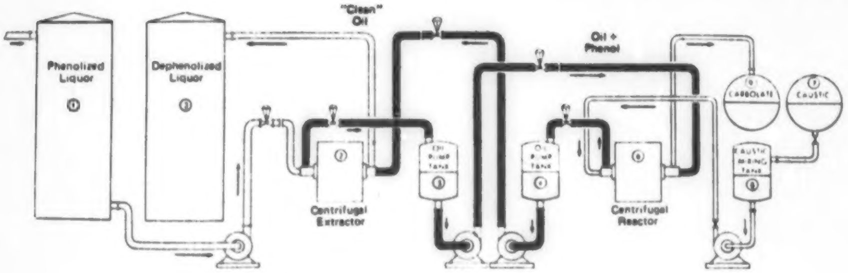
f) Manufacture of fine chemicals and pharmaceuticals.

g) Dehydration of acetic acid.

h) Acetic acid recovery by neutral sulfite semi-chemical pulping plants and cellulose acetate plants. Ketones, ethers, and esters have been used as the extracting solvents.

2. Waste Treatment Applications

a) Removal of phenol and related compounds from wastewaters is the principal application (Refs. 1, 5-13); applications are to petroleum refinery wastes, coke-oven liquors and phenol resin plant effluents. Extraction reduces phenol concentrations from levels of several percent down to levels of a few parts per million. Removal efficiencies of 90 to 98% are possible in most applications, and with special equipment (e.g., centrifugal and rotating disc contactors) removal efficiencies around 99% have been achieved. Commonly used solvents are crude oil, light oil, benzene, toluene, and "benzol"; less common, but more selective solvents are isopropyl ether, tricresyl phosphate, methyl isobutyl ketone, methylene chloride, and butyl acetate. When crude or light oil is used the phenol is not always covered (i.e., the solvent is not recycled); the phenol is destroyed in downstream operations. Alternatively, extraction with light oil may be followed by phenol recovery via extraction of the oil with caustic; in this case, the phenol is recovered as sodium phenolate. A schematic diagram of this process is shown in Figure 2.

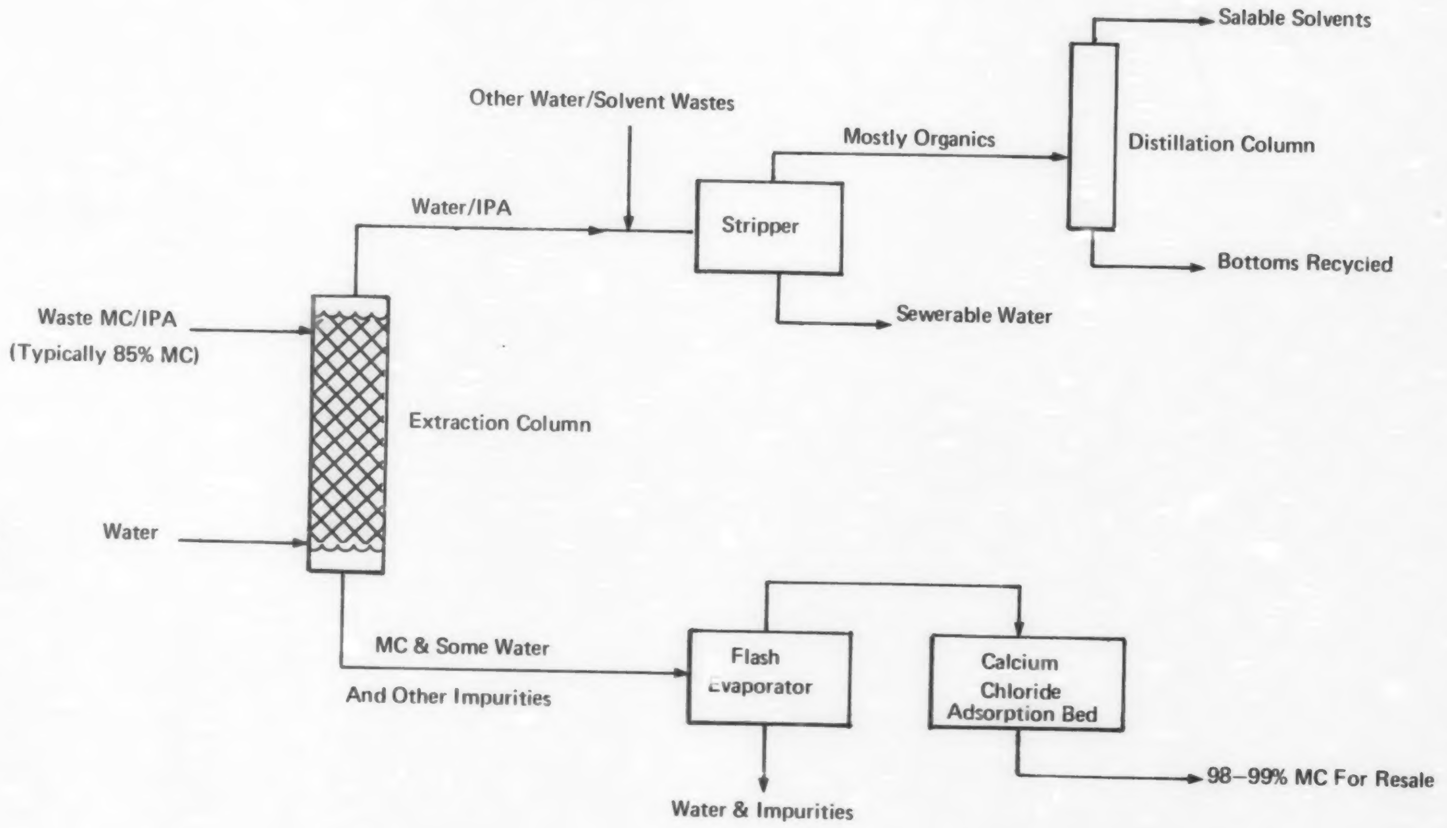

"Clean" Oil
Oil + Phenol
Phenolized Liquor
①
Dephenolized Liquor
③
②
Centrifugal Extractor
Oil Pump Tank
③
Oil Pump Tank
④
⑥
Centrifugal Reactor
Carbolate
Caustic
Caustic Mixing Tank
⑧

Source: Ref. 12.

FIGURE 2 FLOW CHART OF CENTRIFUGAL DEPHENOLIZING PROCESS INVOLVING (1) EXTRACTION OF THE AQUEOUS PHENOLIZED LIQUOR WITH OIL AND (2) SUBSEQUENT EXTRACTION OF THE PHENOL LADEN OIL WITH CAUSTIC
(The oil streams, both "clean" and phenol-laden, are shown by the dark lines.)

b) Solvent recovery via solvent extraction is carried out in at least one hazardous waste management facility (Silresim Chemical Corporation, Lowell, Massachusetts). (See Figure 3.) In one case, waste solvent containing typically 85% methylene chloride (MC) and 15% isopropyl alcohol (IPA) is extracted with water to remove the IPA. Extraction has been carried out in a counter-current column (1 ft diameter, 40 ft high, packed with Berl saddles) which accepts a feed of 1 gpm and produces a purified MC product at around 0.7 - 0.8 gpm. The water/feed ratio used in this device was about 3:1. More recently a single tank has been used as a combination mixer-settler to handle larger flows. The partially purified MC is then further processed through a flash evaporator and calcium chloride absorption bed (for drying) to obtain salable quality MC (98-99%) pure.

A second example involves the reclamation of Freon solvents. The waste material arrives as a mixture of oil, Freon, and other solvents (e.g., acetone or alcohol); distillation separates out the oil (for use as a fuel), but leaves a Freon/acetone (or alcohol) mixture which is then extracted with water to recover Freon. The material is sold for about half the price (per gallon) for new Freon solvent.


Waste MC/IPA
(Typically 85% MC)
Water
Extraction Column
Water/IPA
Other Water/Solvent Wastes
Stripper
Mostly Organics
Sewerable Water
Distillation Column
Salable Solvents
Bottoms Recycled
MC & Some Water
And Other Impurities
Flash
Evaporator
Water & Impurities
Calcium
Chloride
Adsorption Bed
98–99% MC For Resale

Source: Personal Communication From Silresim Chemical Corporation, Lowell, Massachusetts.

FIGURE 3 RECOVERY OF SALABLE METHYLENE CHLORIDE (MC) VIA SOLVENT EXTRACTION FROM A METHYLENE CHLORIDE/ISOPROPYL ALCOHOL (IPA) WASTE

A third example involves the removal of water-soluble solvents (e.g., alcohols) from a waste of mixed chlorinated hydrocarbon solvents via extraction with water. Simple mixer-settlers are commonly used, and the process yields a salable quality (mixed) chlorinated hydrocarbon solvent.

c) Extraction of thiazole-based chemicals from a rubber processing effluent with benzene (Ref. 5).

d) Extraction of salicylic and other hydroxy-aromatic acids from a wastewater using methyl-isobutyl-ketone as the solvent (Ref. 5).

e) Deoiling of quench waters from petroleum operations via solvent extraction has been developed by Gulf Oil Corporation (Ref. 1). The quench water containing about 6000 ppm of dissolved and emulsified oil is extracted with a light aromatic oil solvent and the extract recycled for refinery processing. Additional treatment of the water (e.g., via coalescence) is necessary for water reuse. It is not known if this process is in current use.

f) Recovery of acetic acid from industrial wastewaters (Refs. 14-16). Hydroscience* is proposing a novel extraction to handle wastewaters that may contain acetic acid levels of 0.5% to over 5%. The extractant used is a solution of trioctylphosphine oxide in a carrier solvent. This process is currently in the developmental stage, but has been demonstrated to be practical.

g) A novel process employing solvent extraction is currently being developed by Resources Conservation Co. (Renton, Wash.) to remove essentially all of the water and oils from inorganic and organic sludges (Refs. 17-18). The process, called Basic Extractive Sludge Treatment (B.E.S.T.), converts sludges with .05% to 60% solids to output streams of (1) very dry solids (4-5% mosture), (2) a clear water effluent, and (3) recovered oils, if present in the original sludge. The process train (see Figure 4) includes: (1) extraction of water (and oils) from the sludge with an aliphatic amine at low temperatures (~ 50°F), (2) removal of solids with a centrifuge followed by solids drying (and solvent recovery), (3) heating the solvent/water/oil mixture (to ~ 120°F) to force phase separation, (4) steam stripping of the water phase for solvent recovery, and (5) distillation of the solvent phase for oil recovery. The company claims the process is economical; it requires, for example, only 6400 Btu's per pound to reduce a 7 percent sludge to dry solids versus 15,000 Btu's per pound for conventional high-temperature "brute force" drying methods. A mobile test and demonstration facility has been constructed which can treat 1500 gpd. Several different types of sludges have been successfully processed.

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*Hydroscience Environmental Systems, Knoxville, Tennessee.

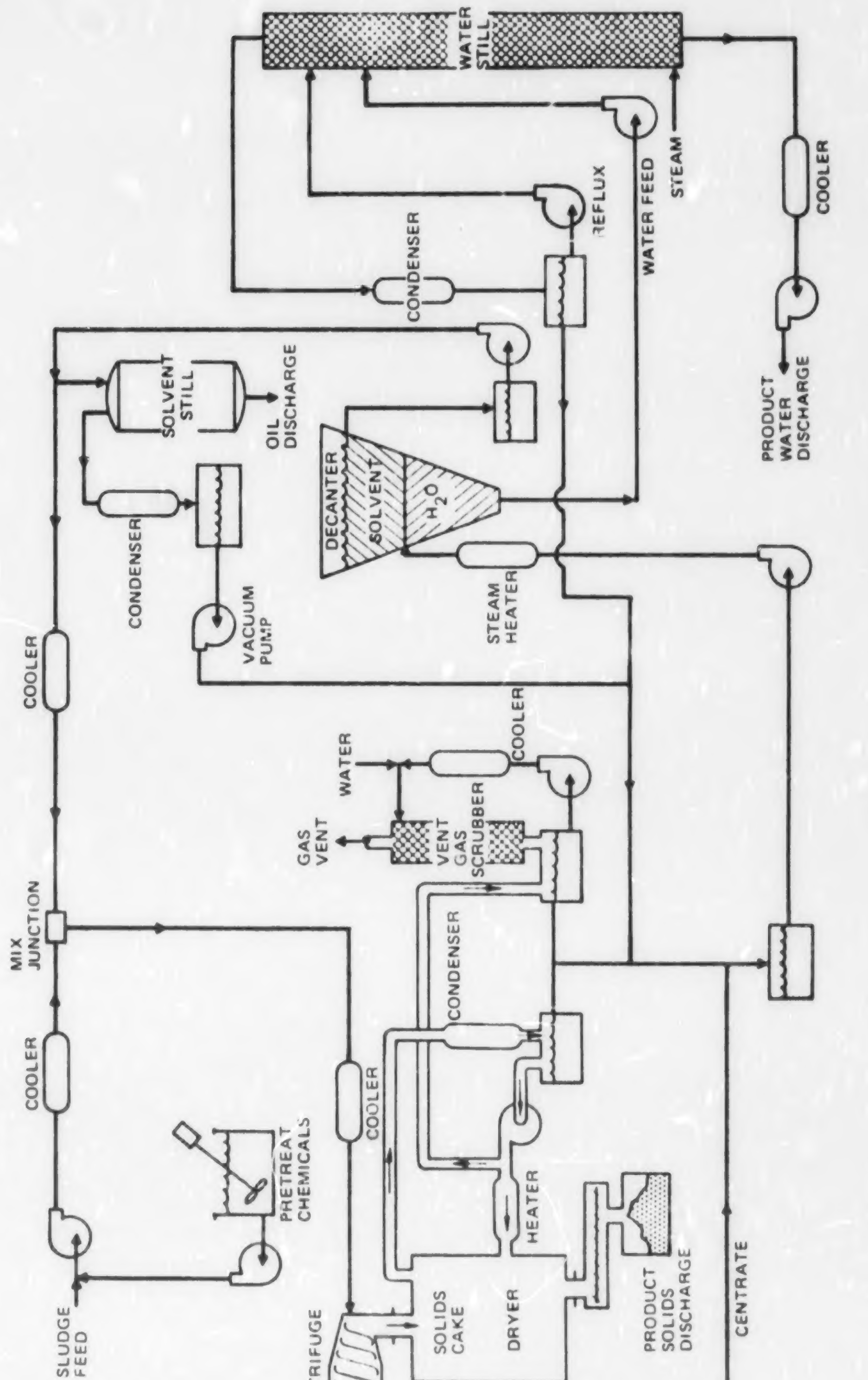

SLUDGE FEED
PRETREAT CHEMICALS
COOLER
MIX JUNCTION
COOLER
CONDENSER
VACUUM PUMP
SOLVENT STILL
OIL DISCHARGE
DECANTER
SOLVENT
H2O
STEAM HEATER
CONDENSER
REFLUX
WATER FEED
STEAM
WATER STILL
COOLER
PRODUCT WATER DISCHARGE
CENTRIFUGE
COOLER
SOLIDS CAKE
DRYER
HEATER
CONDENSER
PRODUCT SOLIDS DISCHARGE
CENTRATE
GAS VENT
VENT GAS SCRUBBER
WATER
COOLER

FIGURE 4 B.E.S.T. PROCESS FOR SOLVENT EXTRACTING WATER AND OIL FROM SLUDGES

Source: Ref. 18.

3. Waste Treatment Applications Investigated by the U.S. Environmental Protection Agency

Five contracts for the investigation of solvent extraction as a wastewater treatment process have recently been funded by the U.S. Environmental Protection Agency (Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma). Each is briefly described below. A background report has been published (Ref. 18).

a) *University of California at Berkeley (Dr. C. Judson King, P.I.)*

In one recently completed contract, Dr. King investigated the feasibility of using volatile solvents (e.g., isobutane or isobutylene) for the extraction of organics from large-flow wastewaters. The extraction is carried out at 40 to 50 pounds pressure; the solvent/solute stream is then flashed down to atmospheric pressure for solute removal. Extraction of a range of chemicals, for the wastewaters of seven to eight industries, was attempted; many of the chemicals were not amenable to biological treatment. A dual solvent approach was also investigated whereby a more polar, less volatile solvent was used for the original extraction and then itself removed from the treated water with the more volatile solvent.

b) *University of California at Berkeley (Dr. C. Judson King, P.I.)*

A second contract, started in the summer of 1975, involves an investigation of the potential for solvent extraction to purify wastewaters resulting from the manufacture of acetic acid. These wastewaters contain significant amounts of oxygenated organics and, in one manufacturing process, chlorinated hydrocarbons. The prospects for a practical and economical system are less clear than usual in this case because of the higher-than-normal water solubility of the solute chemicals.

c) *Union Carbide Corporation (George Somekh, P.I.; Frank Rugg, Manager)*

Union Carbide has a two-year contract (started in May, 1975) to investigate the potential for the extraction of caprolactam and acrylonitrile/acetonitrile from manufacturing plant wastewaters. Based on previous in-house work, Union Carbide feels that the specific solvent extraction process they will test has potential applicability. (Details of the process are not currently available pending patent applications.) The company claims lower energy requirements for their solvent extraction process in comparison with an evaporation/distillation process; capital investment costs may be somewhat higher. The waste streams to be treated will contain less than 1% organics and they will be reduced to ppm levels following solvent extraction.

d) *Gulf South Research (Dr. E. Klein, P.I.)*

Gulf South Research is conducting a research effort, jointly funded by the EPA and eight companies (manufacturers of chlorinated hydrocarbons), to investigate the potential of five processes for the removal of certain wastes, primarily C_2 to C_4 chlorinated hydrocarbons, from industrial effluents. They are investigating steam stripping, activated carbon, biological degradation, ozonation, and solvent extraction; all, except ozonation, have been carried through the pilot stage. For solvent extraction they are investigating the use of a pulsed counter-current column with a C_{10} to C_{16} hydrocarbon cut as the solvent. The research program is expected to be completed in about one year.

e) *Texas A & M (Dr. R.R. Davidson, P.I.)*

This contract called for an assessment of solvent extraction for the removal of light chlorinated hydrocarbons in petrochemical manufacturing wastewaters. In this case, a C_{12} to C_{13} paraffin cut was used as the solvent. Bench scale studies were carried out. The studies showed that solvent extraction was not the best way to remove the chlorinated hydrocarbon contaminants.

Earlier studies funded by the EPA included an investigation of (1) the possibility of treating sewage plant effluents by solvent extraction (Ref. 19) and (2) the possibility of removing glycols from industrial wastewaters containing high salt concentrations (Ref. 20). In the latter study, solvent extraction of the glycol wastewater with secondary or tertiary amines produced a raffinate that was salt-saturated and low in glycol and a product enriched in the glycol and nearly free of salt. The required large solvent-to-feed ratio, the requirement for near-freezing temperatures, and the high reflux to produce a pure product, made solvent extraction, as a treatment method, uneconomical.

B. POTENTIAL APPLICATIONS TO WASTE TREATMENT

1. Treatment of Aqueous Wastes

In actual considerations of aqueous waste treatment, solvent extraction will most often be competitive with steam stripping, and to a lesser degree, adsorption. Solvent extraction will never be competitive with biological treatment, and thus, extraction should be considered only for refractory chemicals (i.e., non-biodegradable chemicals) or in situations where biological treatment is ruled out for some other reason.

Carbon adsorption will tend to be more economical in the treatment of dilute waste streams unless the value of the recovered waste is high. (In general, a hazardous waste is not recovered following removal by carbon adsorption.) As the waste stream to be treated becomes more concentrated, both solvent extraction and steam stripping become more competitive because their economics are less concentration-dependent than carbon adsorption; the costs of frequent carbon regeneration become almost prohibitive in the treatment of concentrated waste streams.

Solvent extraction will be favored over steam stripping (1) for the removal of high molecular weight chemicals (with which steam stripping may have difficulty),

(2) when energy requirements are a determining factor (solvent extraction requires less energy), and (3) when steam stripping is hindered by the formation of azeotropes.

Economic considerations will usually require a low-cost solvent (or negligible solvent losses) and the recovered solute(s) to have some economic value to offset process costs. Two examples are the recovery of phenol and acetic acid from wastewaters where influent concentrations are usually in the range of several hundred ppm to a few percent. Possible future examples include: (1) the recovery of tetrahydrofuran from a tetrahydrofuran/water waste mixture by extraction with toluene, the latter being separated from the tetrahydrofuran in a still; (2) the recovery of dimethylformamide from a dimethylformamide/water waste mixture by extraction with methylene chloride, the latter being separated from the dimethylformamide in a still; and (3) the treatment, for solvent recovery, of other water/solvent wastes such as those that result following steam regeneration of activated carbon (or resin) adsorbents used in vapor phase applications.

2. Treatment of Organic Wastes

Solvent extraction of liquid organic wastes will be attractive if (1) the wastes contain components that may be separated by solvent extraction and (2) distillation is impractical because of azeotrope formation or other problems. Existing applications are based on the removal of water-soluble organic components, using water as the solvent, from halocarbon solvents. There may be real economic incentives for such treatment since solvents costs are very low and a resalable-quality halocarbon solvent results. Further applications will probably have to fit in a similar mold.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Energy consumption for solvent extraction processes will be minimal if solvent extraction is the only unit process involved, e.g., electrical requirements for feed and solvent pumps, and possibly a stirrer or column agitator. One possible exception would the use of centrifugal extractors which have relatively high electrical demands per unit throughput; for example, two makes of centrifugal extractors that have maximum total throughputs of about 500 gpm require electrical motors of 25 and 100 HP.

When the overall process also involves solvent and solute recovery (stripping, distillation, or adsorption), then significant amounts of additional energy (steam and electricity) will be required for such units. Energy requirements for these other unit processes are given in other parts of this manual where the process is featured.

It is estimated that solvent extraction may be less energy intensive than steam stripping, a competing process, especially when the material to be removed by stripping comprises a major fraction of the feed solution.

B. ENVIRONMENTAL IMPACTS

There are no major environmental impacts associated with the proper use of solvent extraction. Solvent extraction will almost always be used for material recovery (for resale or reuse) and thus, will be of some benefit.

When one (or several) solute is recovered from aqueous wastes, minor impacts will result from small losses of the solvent (to the air and/or water), and heat (e.g., from stripping or distillation). In addition, solvent extraction systems seldom produce a raffinate that is suitable for direct discharge to surface waters and thus, a polishing treatment is generally required; biological treatment may suffice in many cases.

When mixed organic liquids are treated principally for the recovery of just one component (e.g., the more valuable halogenated hydrocarbons), current economic forces may make the purification of the other components (as required for resale or reuse) impractical and thus result in a waste for disposal.

C. ECONOMIC ANALYSIS

It is quite difficult to generalize about the costs of solvent extraction because of the wide variety of systems, feed streams, and equipment that may be involved. Some examples of actual or estimated costs of phenol recovery from aqueous wastes are given below. Estimates for acetic acid recovery and comments on cost factors in recovery from organic wastes are also provided.

1. Cost Example: Extraction of Phenol from Aqueous Wastes with Toluene

Capital and operating costs estimates for a complete system for the extraction and recovery of phenol from an aqueous waste stream are given in Table 3. The complete system is diagramed in Figure 5. Some pertinent details are given below:

Water/Phenol Feed:	45,000 lbs/hr containing 1.5% phenol (by weight) Temperature is 110°F.
Toluene Feed:	45,000 lbs/hr (containing ~ 20 ppm phenol from recycle)
Discharge Water:	Contains 75 ppm phenol
Extraction Column:	Rotating disc type; 6 ft diam., 60 ft high; made from carbon steel; contains 50 compartments and equivalent of about 5 theoretical stages. [Equilibrium distribution coefficient of phenol between toluene and water is about 2.] Column cost is $150,000 (FOB); this does not include any costs associated with pumps, stripper, still, or holding tanks.
Loss of Toluene/ Cycle:	Approximately 0.1% per cycle
Electrical Requirements (column only):	One 10 HP electric motor

2. Costs for Other Systems for the Extraction and Recovery of Phenol

The influence of phenol concentration on costs is clearly shown by one recent estimate (Ref. 14) which showed operating costs for a hypothetical extraction system to rise from $0.02/lb. of phenol recovered with an influent containing 1% phenol, to $0.17/lb. of phenol with a 0.1% influent, and to $1.68/lb. of phenol with a 0.01% influent. Since phenol currently costs about $0.30/lb, it is clear that recovery (according to the above estimates) would not be economical for influent concentrations much less than 0.1% phenol (1000 ppm). The process will, of course, work at lower concentrations, and the credit from the recovered phenol will partially offset the process costs.

One other estimate (in 1971) for a similar system put total capital costs at $400,000 and total operating costs at $200,000/year for a 100,000 gpd unit (Ref.1). In this example, benzene was used as the solvent (1:1 ratio of solvent to feed) to recover 5000 lbs/day of phenol from an influent containing 0.5% phenol. The raffinate would contain 10 ppm phenol. Total operating costs in this case work out to $5.80/1000 gallons and are reduced to $2.90/1000 gallons after credit for phenol recovery is taken.

TABLE 3

ESTIMATED CAPITAL AND OPERATING COSTS FOR THE EXTRACTION AND RECOVERY OF PHENOL FROM AN AQUEOUS STREAM

Basis: 45,000 lbs/hr of 1.5% phenol in water; operation 330 days/yr, and 24 hrs/day
Estimated Capital Investment: $800,000

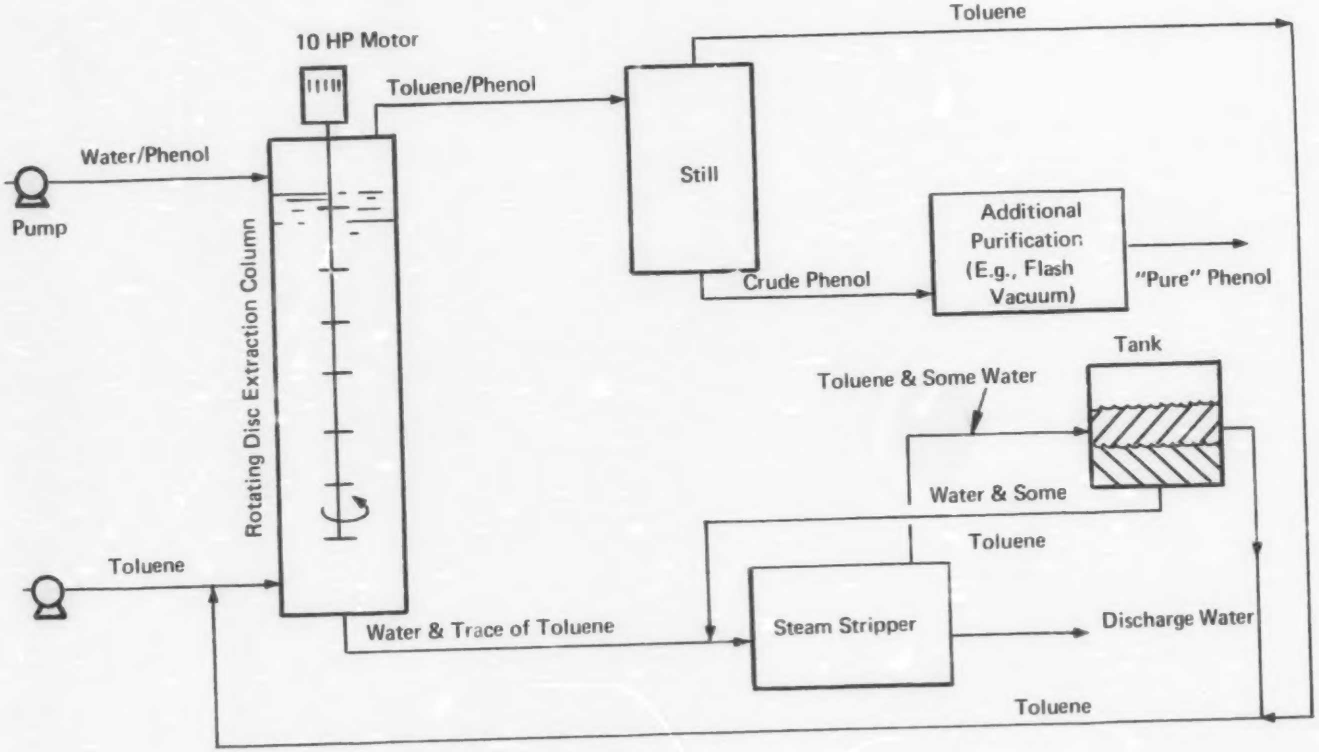
	Annual Quantity	Cost per Unit Quantity	Annual Cost ($)
Variable Costs			
Labor	12,000 hrs.	$12/hr	$144,000
Maintenance (3% of Inv.)			24,000
Electricity	150,000 kWh	$0.02/kWh	3,000
Steam	33 x 10^6 lbs	$4.00/$10^3$ lb	132,000
Toluene	15,000 gallons	$0.61/gallon	9,000
TOTAL VARIABLE COSTS			312,000
Fixed Costs			
Taxes and Insurance (2% of Inv.)			16,000
Capital Recovery (10% – 10 yrs)			132,000
TOTAL FIXED COSTS			148,000
TOTAL ANNUAL COSTS			460,000
Unit Costs – ($1,000 gallons)			10.76
Unit Costs – ($/lb phenol recovered)*			0.0865

*Current selling price of phenol is 26¢/lb; this leads to an annual credit of $1,390,000.

Source: Arthur D. Little, Inc., estimates

3. Phenol Extraction without Recovery

Refinery foul water containing about 300 ppm phenol is often extracted with crude oil with no subsequent phenol recovery. A high oil-to-water ratio may be used (7:1 to 20:1) and high temperatures are sometimes used. Electrical coalescers are sometimes used to aid phase separation. The effluent water has about 90% of the phenol removed and contains 20 to 30 ppm of oil. Operating costs of such treatment have been given (in 1971) as roughly 0.5 mil ($0.0005) per 1000 gallons of oil (Ref. 6).



10 HP Motor
Toluene/Phenol
Still
Toluene
Water/Phenol
Pump
Additional Purification (E.g., Flash Vacuum)
"Pure" Phenol
Crude Phenol
Rotating Disc Extraction Column
Tank
Toluene & Some Water
Water & Some Toluene
Toluene
Steam Stripper
Discharge Water
Water & Trace of Toluene
Toluene

FIGURE 5 EXAMPLE OF LIQUID-LIQUID SOLVENT EXTRACTION OF ORGANICS: REMOVAL OF PHENOL FROM WATER WITH TOLUENE

4. Extraction and Recovery of Acetic Acid

Cost estimates for the extraction and recovery of acetic acid from aqueous solution have recently been given (Ref. 16) for two different systems: (1) extraction with trioctylphosphine oxide (TOPO) which is dissolved in a carrier solvent, and (2) extraction with diethyl ether. The stream characteristics chosen for a cost comparison between these two systems were: flow, 200 gpm; and acetic acid concentration, 3%. Capital and operating costs are summarized in Table 4 below.

TABLE 4

COST COMPARISON FOR EXTRACTION AND RECOVERY OF ACETIC ACID FROM WATER

	Solvent Extraction Using TOPO	Solvent Extraction Using Ether
Capital Costs	$2,000,000	$3,200,000
Total Operating Costs (¢/lb of acetic acid)	0.068*	0.089**

*Equivalent to $.17/1000 gallons of water
**Equivalent to $.23/1000 gallons of water

Source: Ref. 16

Since acetic acid is currently worth about $.15/lb, both systems will eventually return a profit.

5. Extraction and Recovery of Solvents from Waste Organic Liquids

Extraction, with water, of the hydrophylic component from a waste solvent solution containing both hydrophylic and hydrophobic components, may be quite inexpensive since current practice at one facility indicates that a single tank can be used as a combination mixer-settler. Mixing may be carried out with a recirculating pump system. It is likely that many facilities will already have such equipment available (or could obtain such, second hand, at very low cost) and, thus, capital costs will be negligible. Operating costs, mainly labor and electricity, will not be large.

The major costs of a whole process for reclaiming a solvent from such a mixture will be related to other unit processes which may be needed, e.g., evaporation, distillation, etc., as shown in Figure 3. Additionally, while some wastes may be obtained for free or even with a payment for "disposal," other wastes that clearly contain a recoverable, valuable product may have to be purchased. Because of the diversity of situations which may arise, no meaningful cost figures for such applications of solvent extraction can be given.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Solvent extraction should be regarded as a process for treating concentrated, selected, and segregated waste streams primarily where material recovery is possible to offset process costs. Solvent extraction, when carried out on the more concentrated waste streams will seldom produce a treated effluent (the raffinate) that can be directly discharged to surface waters; some form of final polishing will usually be needed. Solvent extraction cannot compete economically with biological oxidation or adsorption in the treatment of large quantities of very dilute wastes, and it will have trouble competing with steam stripping in the recovery of volatile solutes present in moderate to low concentrations.

Nevertheless, solvent extraction is a proven method for the recovery of organics from liquid solutions and will be the process of choice in some cases. Table 5 summarizes the areas of actual and potential applicability.

TABLE 5

AREAS OF ACTUAL AND POTENTIAL APPLICABILITY OF SOLVENT EXTRACTION FOR ORGANICS REMOVAL AND RECOVERY

- **Wastes that have been treated**

Physical Form	**Solute Recovered**
Aqueous Solution*	– Phenol – Acetic acid – Salicylic and other hydroxy aromatic acids – Petroleum oils
Organic Solution*	– Methylene chloride from isopropyl alcohol – Freon from oil and alcohol (or acetone) – Mixed chlorinated hydrocarbons from alcohol or acetone

- **Wastes that might be treated**

Physical Form	**Solute Recovered**
Aqueous Solutions* (containing one or just a few solutes)	– Any valuable organic solute present in moderate to high concentration. Candidates might include phenols, acids, alcohols, amines, glycols, tetrahydrofuran, dimethylformamide, and others.
Organic Solutions* (containing a mixture of water soluble and non-water-soluble components)	– Will often be able to recover both water-soluble and non-water-soluble components. Water-soluble components include low molecular weight alcohols, ketones, amines, ethers phenols, etc. Non-water-soluble components include simple hydrocarbons, halogenated hydrocarbons, oils, and other *high* molecular weight organics which may contain a hydrophylic functional group.

*Some degree of emulsification and suspended solids may be tolerated.

There are relatively few insurmountable technical problems with solvent extraction. The most difficult problem is usually finding a solvent that best meets a long list of desired qualities including low cost, high extraction efficiency, low solubility in the raffinate, easy separation from the solute, adequate density difference with raffinate, no tendency for emulsion formation, non-reactive, and non-hazardous. No one solvent will meet all the desired criteria and, thus, compromise is necessary. There is a wide range of extraction equipment available today, and space requirements are not a problem.

Process costs are always a determining factor with solvent extraction, and they have thus far limited actual applications to situations where a valuable product is recovered in sufficient quantity to offset extraction costs. These costs will be relatively small when a single-stage extraction unit can be used (e.g., a simple mixer-settler) and where solvent and solute recovery can be carried out efficiently. In certain cases, the process may yield a profit when credit for recovered material is taken. Any extraction requiring more than the equivalent of about ten theoretical stages may require custom-designed equipment and will, thus, be quite expensive.

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B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD (PARTIAL LISTING)

The authors of the recent literature cited in Subsection A above may be contacted for further information on the specific applications discussed. Below are listed a few other individuals or organizations that will be able to provide some additional information.

1. Leon H. Myers, Acting Chief, Petroleum-Organic Chemicals Waste Section, U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma. (Contact for information on recent EPA-funded contracts for solvent extraction investigations.)

2. Dr. C. Judson King, University of California at Berkeley (Project Director on current EPA solvent extraction contract).

3. Dr. John Miserlis, Silresim Chemical Corporation, Lowell, Massachusetts. (Company uses solvent extraction for recovery of organic solvents from mixed organic wastes.)

4. Dr. R.R. Davidson, Texas A & M University, College Station, Texas (Project Director on recent EPA solvent extraction contract).

5. Mr. Ed Poppele, York Process Equipment Company, Parsippany, New Jersey. (Company designs and manufactures liquid-liquid extraction columns.)

6. Mr. Steve Rubin and Dr. George Schwake, Centrico, Inc., Northvale, New Jersey. (Company assembles and distributes the Westphalia centrifugal extractors.)

7. Dr. R.D. Fox, Hydroscience, Inc., Knoxville, Tennessee. (Company has patented process for the recovery of acetic acid, or other organic acids, from water via liquid-liquid extraction.)

MICROWAVE DISCHARGE

Prepared by

Joan B. Berkowitz

I. CONCLUSIONS AND RECOMMENDATIONS

- Chemical reactions in plasmas have been studied in university and industrial laboratories for many years, but few commercial applications have emerged, and those that do exist involve high cost, high-value-added products.

- Microwave discharge treatment of hazardous waste liquids and vapors in oxygen plasmas is currently in the research stage. Early results are very promising.

- We recommend that laboratory and pilot-scale testing be extended to relatively small-volume highly toxic industrial waste streams, which present particularly difficult problems for disposal.

II. PROCESS DESCRIPTION

A. BACKGROUND AND UNDERLYING PRINCIPLES

The proposed use of a microwave discharge in the treatment of hazardous wastes (Ref. 1) is a special application in the general field of plasma chemistry. A plasma is a partially ionized gas composed of ions, electrons, and neutral species. A plasma can be produced in several ways, the most common of which is a gaseous electric discharge. In a discharge, free electrons produced by a random or deliberate process, pick up energy from an imposed electric field and transfer this energy, by collisions, to neutral gas molecules. The resultant molecular excitation leads to the formation of a variety of metastable, atomic, free radical, and ionic species. These species are all chemically reactive, and under steady state plasma conditions, generation and recombination of the active species will proceed simultaneously. Plasmas produced by electric discharges have been used more for chemical synthesis of new stable compounds than for molecular decomposition. That is the plasmas have been run under conditions where the excited decomposition products serve as intermediates in the formation of stable end-products, often of higher molecular weight than the starting material. In oxygen plasmas, however, particularly under conditions of high power density, decomposition products are typically oxidized to stable compounds similar to those obtained in complete combustion (e.g., water and CO_2 in the case of hydrocarbon feeds).

The field of plasma chemistry dates back to at least 1796, when four Dutch chemists reported that an oily substance was produced by the action of spark discharges on ethylene (Ref. 2). The field lay dormant until the latter half of the 19th century when silent discharges became available. (Ozonizers (see Ozonation report) are one type of silent discharge.) In 1874, it was shown (Ref. 3) that acetylene reacted rapidly and completely in a discharge to form a hard, brittle, insoluble amorphous solid. In 1907, CS_2 was subjected to a silent discharge, yielding "a black substance" (Ref. 3). In 1910, Dewar and Jones passed CS_2 vapor through an ozonizer and froze out the CS radical in a liquid air cooled trap (Ref. 3). On heating, it polymerized rapidly.

In the 1920's and 30's, much work was done in plasma chemistry, using high-voltage glow discharge tubes. It was shown that ethylene vapor injected into an evacuated electric discharge chamber yielded butylene, acetylene, and polyethylene liquids; heptane yielded hydrogen and a yellowish brown solid; benzene vapor yielded a resinous product, etc.

This early work was limited by available discharges, which were either dc or low-frequency ac and required electrodes in the discharge chamber. Plasma chemistry remained a laboratory curiosity until the development of radar made possible high frequency power discharges in the microwave region (1,000-10,000 MHz). The first use of a microwave apparatus for molecular decomposition is ascribed to Nagle, who in 1947 found it a convenient method for producing atomic hydrogen (Ref. 3). Since the space program, the plasma torch or plasma jet, which uses dc, low-frequency ac, or high-frequency microwave fields to maintain a high temperature plasma, has provided a new tool for studying chemical interactions at even higher degrees of ionization than are possible with the microwave discharge.

B. OPERATING CHARACTERISTICS

1. Feed Streams

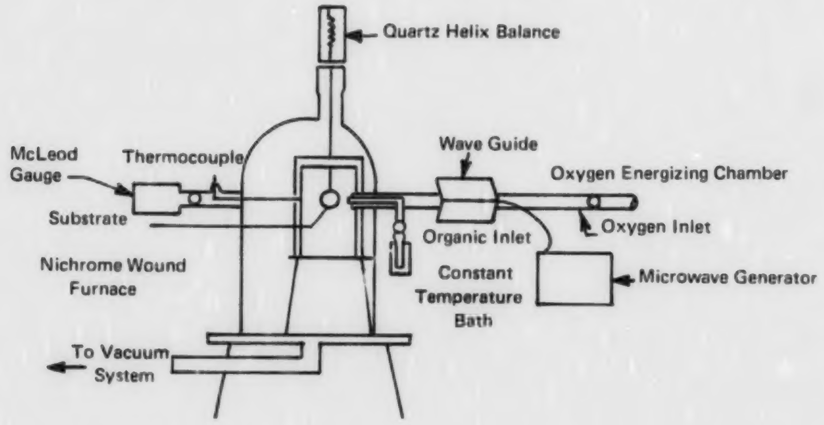
Plasmas can be initiated only in gases, but in gases of all kinds–inert gases (e.g., Ar, He), permanent gases (e.g., N_2, Cl_2, O_2, H_2, CO), inorganic vapors (e.g., H_2O, CO_2, $TiCl_4$, BCl_3, HCN, PF_3), organic vapors, and gaseous mixtures. Solids and liquids exposed to the reactive species in plasmas, particularly permanent gas plasmas, have also been shown to undergo chemical change. In most studies of the reactions of condensed phases with plasmas, the solids or low vapor pressure liquids are merely placed in the discharge chamber. In recent work being carried out at Lockheed, organic and organo-metallic liquids have been drop fed by gravity onto quartz mesh fibers positioned at the center of the plasma zone. This essentially improves the contact between the plasma and the condensed phase, and allows the introduction of large amounts of liquid without dismantling the apparatus.

2. Apparatus

The basic elements of a microwave discharge reactor are: (a) a microwave generator or source of power; (b) a waveguide which leads the microwave power from the generator to a resonant cavity, which surrounds the reactor (c) a reaction chamber, which must be made of silica or quartz to minimize dielectric losses; (d) a system for generating or feeding vapors, or reactants or condensed phases into the reaction chamber; (e) a system for controlling pressure and flow; and (f) a system for collecting reaction products.

Specific reactor designs can vary considerably, depending upon the application. Detailed equipment and apparatus descriptions are provided in the literature (Refs. 2-4). Schematic diagrams illustrating the general principles and the range of applications are given in Figures 1 and 2, and are discussed briefly below.

Figure 1 shows an apparatus used by Secrist of IBM and Mackenzie of RPI (Ref. 4) to study decomposition of metal-organic compounds in an oxygen plasma and subsequent deposition of amorphous metal oxide films outside of the discharge region. The oxygen plasma was generated with a commercial Raytheon PGM-10 Microwave Generator, capable of supplying 100 watts of microwave energy at 2450 MHz. Excited oxygen and metal organic vapors were introduced into a bell jar, containing a weighed sodium chloride substrate, heated to 200°C by a surrounding furnace. The metal-organic liquids were contained in a graduated cylinder, surrounded by a constant temperature bath for control of vapor pressure and rate of introduction of the organometallic vapors. System pressures were typically 0.24 torr with gas flow rates of 1.76 cc/min. Films of SiO_2, GeO_2, B_2O_3, TiO_2 and SnO_2 were deposited at a rate of about 20 A/min by respective decomposition of tetraethoxy-silane, germane, and borane, titanium tetra-isopropylate, and dibutylene diacetate via an oxygen plasma. Decomposition of $(C_2H_5)_4$ Si via a nitrogen plasma led to deposition of amorphous silicon nitride. No information is given with respect to the fate of the organic constituents of the reactants, but presumably they are or could be converted to CO_2 and water vapor.


Quartz Helix Balance
McLeod Gauge
Thermocouple
Wave Guide
Oxygen Energizing Chamber
Substrate
Oxygen Inlet
Organic Inlet
Nichrome Wound Furnace
Constant Temperature Bath
Microwave Generator
To Vacuum System

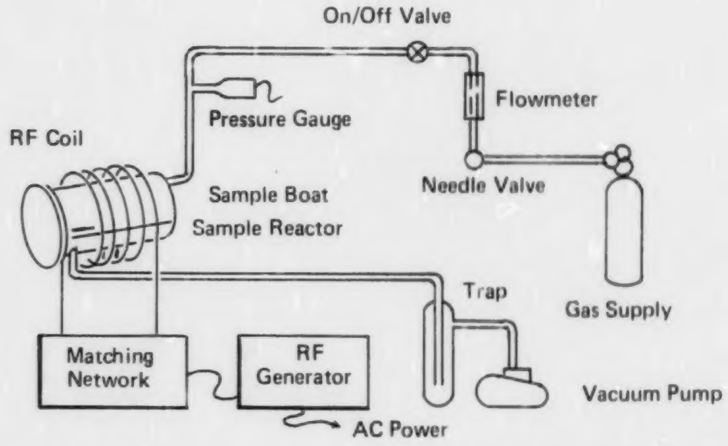
Source: Secrist and MacKenzie, Ref. 4

FIGURE 1 SCHEMATIC OF MICROWAVE DISCHARGE APPARATUS FOR DEPOSITION OF OXIDE FILMS

Figure 2 is an apparatus used in analytical chemistry for ashing of samples. The advantage of an oxygen plasma for ashing purposes is that it degrades organic materials, leaving inorganic residues, at temperatures below 300°C. As shown, the sample to be treated is inserted into the plasma reactor chamber. Oxygen flow rates are typically 50-300 cc/min (STP) and operating pressures are in the range of 0.5 to 1.5 torr. The plasma is initiated and the reaction allowed to proceed to completion. Samples may be solid powders, flat sheets, films, foams, porous materials, or low vapor pressure liquids or semisolids. Completeness of oxidation of the organics can be gauged approximately by the change in color of the plasma from blue (when CO and CO_2 are present) to pink (pure oxygen plasma). In this application, an RF plasma is used. Although organic materials are completely oxidized, the sample size is limited by the general non-uniformity of Rf plasmas, as compared with microwave plasmas.

3. Output Streams

One of the major problems in the use of microwave plasmas for the treatment of hazardous wastes has been that the results are not predictable. The term microwave plasma "decomposition," which is sometimes used, is misleading. As traditionally carried out reactions in plasmas are as likely to lead to association products as to dissociation products, and the association products can be toxic. The problem has recently been overcome, however, through the use of intense oxygen plasmas that effectively bring about complete combustion of organics at low ambient temperatures. In other words, in an oxygen plasma at high power densities, rates of oxidation of dissociated species can be more rapid than rates of recombination.



Source: Ref. 2.

FIGURE 2 SYSTEM COMPONENTS FOR PLASMA-ASHING SAMPLES PRIOR TO ANALYSIS

Because hazardous wastes are unpredictable and inconstant in composition, considerable research will be required to assure the reliability of microwave discharge techniques for detoxification. In one of the first studies of the use of microwave to treat hazardous wastes, Lockheed used a 2450-MHz microwave power source delivering up to 2.5 kW to study the plasma decomposition of DIMP (diisopropyl methyl phosphonate) and DMMP (dimethyl methyl phosphonate), two compounds associated with nerve gas (Ref. 5). The DIMP and DMMP were introduced into the microwave discharge cavity in a helium or air carrier. Experimental conditions and results are summarized in Table 1. A number referred to by the authors as % conversion, which ranges from 62.4-99.5%, is based on residual DIMP or DMMP. The solid and liquid products even in the air plasma, however, still represent difficult disposal problems: phosphoric acid, methyl phosphonic acids, alcohols, plus unknown black liquids which may not be more suitable for landfill than the original agents.

Although condensed phase products of unknown composition formed from DIMP and DMMP in air plasma, the experiments on oxygen plasma ashing in analytical chemistry suggest that oxygen plasma reactions can be made to proceed essentially as low temperature combustion processes, with end products similar to those of incineration. More recent studies at Lockheed have demonstrated that this is in fact the case for a variety of organophosphorus and halogenated hydrocarbon compounds.

TABLE 1

REACTIONS OF DMMP AND DIMP IN HELIUM AND AIR MICROWAVE PLASMAS

Toxic Agent	Carrier Gas	Power, Watts	Pressure, Torr	Agent Flow Rate, g/hr	Agent Con., g/l carrier	Residence Time, Sec	Results
DMMP	He	50-200	3-55	0.8-4.2	0.06-0.31	1.5-2.4	Yellow solids and some black tarry deposit in the reaction tube; products collected in cold trap: trimethyl phosphite; methanol; less than 0.5% DMMP
DIMP	He	130-210	9-17	1.27-1.75	0.017-0.137	0.26-1.3	Predominant products were solids. Next in importance was a liquifiable gas, probably propylene. Liquid and solid residues had large amounts of H_3PO_4 and lesser amounts of methylphosphoric acid
DMMP	Air	140-510	29-62	0.92-1.28	0.0108-0.0128	0.12-0.15	Solids deposited in the reaction tube and probably contained methylphosphoric or phosphorous acids. A black viscous liquid deposited in the reac. chamber at high pressures, but no solids.
DIMP	Air	125-160	11-82	0.84-1.47	0.0052-0.125	0.13-0.49	Products in discharge tube contained phosphoric and methylphosphoric acid. Liquid products had isopropanol and three unidentified gas chromatograph peaks

Source: Ref. 5

III. APPLICATIONS TO DATE

A. HISTORY OF USE

Studies of chemical reactions in plasmas generally, and in microwave plasmas in particular, have been confined largely to laboratory research investigations. Although much of the research has been done in industry, commercial applications are sparse. A recent book by Hollahan and Bell (Ref. 2) provides an excellent review of the status of applications through 1973. The major commercial interest has centered around polymer film deposition, (6), (7) modification of the surface properties of textiles and polymers, surface hardening of metallic parts in a nitrogen plasma, silver ion plating of vacuum ball bearings, chemical analysis, and semiconductor device fabrication. In the analytical area, plasma techniques are apparently used fairly routinely in preparing samples for microscopic analysis through ashing, etching, replication of metal surfaces by epitaxial oxide formation, and cleaning and hydrophilization of TEM specimen support films. In semiconductor device fabrication, plasma photoresist removal and plasma etching techniques were laboratory curiosities in 1968 and commercial processes three years later. Recently, Lockheed has demonstrated the use of microwave oxygen plasmas for the detoxification of hazardous materials (5A) at throughput rate of 5-10 lbs/hr.

B. PRINCIPAL CURRENT APPLICATIONS

1. Chemical and Physical Analysis

Commercial instruments were introduced in the late 1960's and early 70's for plasma ashing and other analytical applications. The typical sample size for ashing is 0.5 to 10 g; a "large" reactor (16" long and 5" in diameter) will handle samples up to 200 g. R.F. oxygen plasmas are used most commonly. General applications include:

- Recovery of trace metals from organic matrices
- Retrieval of mineral phases from coal samples
- Isolation of organic matter from marine sediments
- Non-destructive removal of organic matter from samples of tooth and bone tissue
- Surface etching
- Ashing for recovery and microscopic analysis of particulates

2. Semiconductor Device Fabrication

a. Photoresist Removal

In the production of semiconductor devices, a layer of photosensitive polymer (photoresist) is applied to the semiconductor substrate, and exposed to optical radiation through a precisely made mask. Following a number of additional steps, the resist must be completely stripped off. This can readily be accomplished at temperatures as low as 40°C by microwave plasma oxidation. Commercial units are available which can process 20,000 semiconductor wafers per week.

b. R.F. Plasma-Etching

One of the final steps in device fabrication is etching of silicon dioxide or silicon nitride diffusion masks to expose areas for electrical contact. Commercial units are available for etching of SiO_2 or Si_3N_4 in a CF_4 plasma. The units can handle 50-60 wafers at a time, and are cleaner, cheaper, safer, and faster to operate than conventional chemical etch baths.

C. POTENTIAL APPLICATIONS TO WASTE TREATMENT

Lockheed, under the auspices of the U.S. EPA, is currently investigating the microwave plasma decomposition of hazardous wastes. Since the program is on-going and no final report has been issued, detailed discussion of preliminary results here would be premature. A Phase I Final Report, issued subsequent to the completion of the present study may be consulted. (5A)

The early Lockheed work was done in a system capable of handling a liquid or vapor feed rate of around 1.1 lb/hr. Complete decomposition in an oxygen plasma has required a power input of approximately 4-5 kW. Lockheed is currently constructing a larger system capable of treating 10-100 lb/hr of feed, with a 50 kW power source.

The Lockheed system is designed to handle organic and metal-organic liquids and vapors. It could possibly be extended to handle fine powders or particulates. With an oxygen plasma, the system is roughly analogous to low temperature incineration. The small capacity of even a large microwave facility certainly precludes general use of the process. There may be specialized applications for small quantities of oxidizable wastes which are not amenable to high temperature incineration.

Experience with RF plasma ashing of samples for analysis suggests that a microwave system might also be technically capable of detoxifying or segregating organic constituents from solids, sludges and tars. The RF analytical systems are only capable of handling 100 gram size samples at most, but a microwave system might be engineered to handle larger quantities.

IV. ENERGY, ENVIRONMENTAL ISSUES, AND ENERGY

A. ENERGY REQUIREMENTS

Lockheed has estimated power requirements from their development data as 1.6 kWh/lb of treated waste. Conversion loss from line power to RF power is 60% and utilization of RF power ranges from 30% to 50% in the resonant cavity, but 90-95% in the trough waveguide applicator developed by Lockheed.

B. ENVIRONMENTAL IMPACTS

Oxygen plasma treatment of halogenated hydrocarbons can give rise to Cl_2O, $COCl_2$, HCl, Br_2, BrO_2, and Br_2O emissions. Nitrogen-containing organics are likely to give rise to nitrogen oxides. Metal fumes are likely to be less of a problem in oxygen microwave plasma systems than in high temperature incinerators.

C. ECONOMIC ANALYSIS

The major capital cost of a microwave system is the cost of the generator. Intermediate power generators in the vicinity of 1kW cost roughly $2-3/W. Above 10 kW, the price drops to around $1-2/W. Thus a 5 kW generator suitable for systems handling about one pound of waste per hour might cost about $10,000-15,000. A 50 kW generator, which Lockheed plans to use in a system handling up to 100 lb/hr of waste, might cost in the neighborhood of $50,000-100,000. There will of course be an additional cost of reactors, ancillary glassware, and other electrical equipment, and pollution control devices.

The major operating costs, apart from capital amortization include labor and maintenance, carrier gases (probably oxygen or steam), and electric utilities. Approximate costs for treating 400,000 lb/yr of wastes are given in Table 2. The figures are extremely rough estimates based on early research efforts which emphasized technical operations. Cost optimization studies should follow.

TABLE 2

ESTIMATED OPERATING COSTS FOR MICROWAVE DISCHARGE

Basis: 400,000 lb/yr of wastes; 330 day/yr operation; 3 shifts

Approximate Capital Investment: $100,000

	Annual Quantity	Cost per Unit Quantity	Annual Cost ($)
Variable Costs			
Operating Labor	8,000 MH	$12/hr	96,000
Maintenance (4% of Inv.)			4,000
Oxygen	1.7×10^6 SCF	$0.005/SCF	8,500
Electricity	640,000 kWh	0.02kWh	12,800
Liquid Oxygen storage			3,000
Total Variable Costs			124,300
Fixed Costs			
Taxes and Insurance (2%/yr)			2,000
Capital Recovery (10 yr-10%)			16,250
Total Fixed Costs			18,250
Total Annual Costs			160,800
Cost per pound of waste treated			0.40

Source: Arthur D. Little, Inc., estimates

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

The outlook for this technique is encouraging, particularly for highly toxic materials that cannot be handled in any other way, or for recovery of high-value components. It is too early to predict the possible range of applications or the specific waste streams which could be treated cost-effectively.

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B. PEOPLE/ORGANIZATION KNOWLEDGEABLE IN THE FIELD

1. Prof. Alexis Bell, U. of California, Chemical Engineering Dept., Berkeley, California.
2. Dr. Lionel J. Bailin, Lockheed Research Laboratory, Palo Alto, California.
3. D.A. Oberacker, EPA, Cincinnati, Ohio.

NEUTRALIZATION

Prepared by

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I. CONCLUSIONS AND RECOMMENDATIONS

Neutralization is a technique of accepted technical and economic feasibility by which certain hazardous wastes can be treated. It is in widespread use in various industries, in many applications. The basic principle behind the process is simple–combining an acid with an alkali to adjust the pH of the product to an acceptable level. In the case of effluent wastes, either excess acidity or excess alkalinity is corrected, bringing the pH to a value between 6.0 and 9.0. There are numerous methods by which the admixture can be accomplished and a multitude of waste streams with diverse chemical and physical characteristics which are treatable by this technique.

The knowledge to implement any neutralization process exists, but must be tailored to needs. We recommend that neutralization be considered as part of every waste treatment facility.

II. PROCESS DESCRIPTION

A. BACKGROUND

Many manufacturing and processing operations produce effluents that are acidic or alkaline in nature. Neutralization of an excessively acidic or basic waste stream is necessary in a variety of situations, for example:

1) to prevent metal corrosion and/or damage to other construction materials,
2) to protect aquatic life and human welfare,
3) as a preliminary treatment, allowing effective operation of biological treatment processes, and
4) to provide neutral pH water for recycle, either as process water or as boiler feed.

Treatment to adjust pH may also be desirable to break emulsions, to insolubilize certain chemical species, or to control chemical reaction rates, e.g., chlorination. Although natural waters may differ widely in pH, changes in a particular pH level could produce detrimental effects on the environment. To minimize any undesirable consequences, the effluent limitations guidelines for industrial sources set the pH limits for most industries between 6.0 and 9.0 for 1977 and 1983.

B. UNDERLYING PRINCIPLES

Simply, the process of neutralization is the interaction of an acid with a base. The typical properties exhibited by acids in solution are due to the hydrogen ion, $[H^+]$. Similarly, alkaline (or basic) properties are a result of the hydroxyl ion, $[OH^-]$. In aqueous solutions, acidity and alkalinity are defined with respect to pH, where $pH = -\log [H^+]$ and, at room temperature, $pH = 14 + \log [OH^-]$. In the strict sense, neutralization is the adjustment of pH to 7, at which level the concentrations of hydrogen and hydroxyl ions are equal. Solutions with excess hydroxyl ion concentration ($pH > 7$) are said to be basic; solutions with excess hydrogen ions ($pH < 7$) are acidic. Since adjustment of the pH to 7 is not often practical or even desirable in waste treatment, the term "neutralization" is sometimes used to describe adjustment of pH to values other than 7.

The actual process of neutralization is accomplished by the addition of an alkaline to an acidic material or by adding an acidic to an alkaline material, as determined by the required final pH. The primary products of the reaction are a salt and water. A simple example of acid-base neutralization is the reaction between hydrochloric acid and sodium hydroxide:

$$HCl + NaOH \rightarrow H_2O + NaCl$$

The product, sodium chloride in aqueous solution, is neutral with pH = 7.0.

C. OPERATING CHARACTERISTICS

1. Feed Streams

Neutralization finds its widest application in the treatment of aqueous wastes—containing strong acids such as sulfuric and hydrochloric, or bases such as caustic soda and ammonium hydroxide. However, the process can be used with non-aqueous materials (for example, acidic phenols, which are insoluble in water). Although neutralization is a liquid phase phenomenon it can also treat both gaseous and solid waste streams. Gases can be handled by absorption in a suitable liquid phase, as in the case of alkali scrubbing of acid vapors. Slurries can be neutralized, with due consideration for the nature of the suspended solid and its dissolution properties. Sludges are also amenable to pH adjustment, but the viscosity of the material complicates the process of physical mixing and contact between acid and alkali which is essential to the treatment. In principle, even tars can be neutralized, although the problems of reagent mixing and contact are usually severe, making the process impractical in most instances. Solids and powders that are acidic or basic salts could also be neutralized if dissolved.

Neutralization can be used to treat both inorganic and organic waste streams that are either excessively acidic or alkaline. A neutralization process often used to precipitate heavy metal ions, e.g., Zn^{++}, Pb^{++}, Hg^{++}, or Cu^{++}, involves addition of an alkali (usually lime) to a waste stream. Organic compounds which can be treated include carboxylic acids, sulfonic acids, phenols, and many other materials.

2. Process Operation

The basic principle behind neutralization is simple—the mixing of an acid with an alkali. Neutralization may be carried out in tanks, in ponds, in absorber columns, or in a variety of other types of reaction equipment either in batch or continuous-flow operations, depending in part upon the volume and rate of flow. Although many different chemicals can be neutralized, certain principles are common to most systems and are independent of specific designs.

The addition of appropriate quantities of neutralizing agent is monitored and adjusted by pH measurement and control. In batch treatment an operator can take samples, measure the pH, and add the required dose of acid or alkali. In a continuous flow system, automatic pH monitors check the acidity or alkalinity and control the feeding of neutralizing agent. The number of neutralization units, and the location of pH sensors are determined by the stability of the waste stream pH. Where widely varying pH levels are experienced, several reaction units plus additional monitoring equipment may be required. A stream with large fluctuations in pH might also be preceded by an equalization basin which would yield a more homogeneous effluent with a narrower pH range for treatment.

The selection of a neutralizing agent is dictated by a number of factors such as economics, availability, and process compatibility. Commonly, the choice of an acid for neutralizing alkaline wastes is between sulfuric acid and hydrochloric acids (Ref. 2). Because of its lower cost, sulfuric acid is usually preferred, but it does entail the possibility of forming relatively insoluble salts, e.g., calcium sulfate, with the attendant problems of scaling and solids handling. The products of neutralization with hydrochloric acid are usually soluble (as are the salts of nitric acid). However, it is important to be cognizant of the legal discharge limits on soluble species which may be added by neutralization.

The choice of alkali for neutralization of an acid is generally between reagents containing sodium, calcium, or magnesium. In the selection of an alkali, an important element is the "basicity factor" which is the number of grams of calcium oxide equivalent in neutralization capacity of a particular alkali (Ref. 1). Solid sodium hydroxide (76% Na_2O) has a basicity factor of 0.687; thus it is somewhat less effective (on a weight basis) than calcium oxide with respect to neutralization. However, caustic soda has the advantage of being very soluble, thus allowing the use of concentrated solutions. In addition, the product salts of neutralization are also highly soluble, precluding any solids problems.

The disadvantage of caustic soda is the relatively high raw material cost. The lime/limestone reagents, such as high-calcium hydrate, $Ca(OH)_2$, high-calcium quicklime, CaO, and high-calcium limestone, $CaCO_3$, have basicity factors of 0.710, 0.941, and 0.489, respectively; they are less expensive than sodium hydroxide, but because of their low solubility, they often require increased capital investment. These solids are usually fed as slurries on the order of 15% solids. In the presence of sulfuric acid, insoluble calcium sulfate is formed, and the accompanying problems of sludge and scale will occur. It should be noted that limestone is the least effective neutralizing agent (on a weight basis) described thus far. Sodium carbonate (soda ash) also has only a moderate basicity factor of 0.507, but it is much more soluble—as are the products.

The use of magnesium in the oxide or carbonate from as a reagent can be beneficial in many instances. In particular, the neutralization of sulfuric acid by a magnesium-based alkali produces a soluble magnesium sulfate (as opposed to the insoluble calcium salt). Magnesium oxide is more effective as a neutralizing agent than calcium oxide (on a weight basis); as is dolomitic quicklime $CaO \cdot MgO$ (basicity factor of 1.110). Also, dolomitic limestone, $CaCO_3 \cdot MgCO_3$, is an improvement (basicity factor of 0.564) over calcium limestone.

In appropriate situations, it may be feasible to use a plant's acid or alkaline waste stream as a neutralizing agent for other effluents. Economically, such reuse of waste materials as acid or alkali reagents is usually superior to other alternatives. In industries producing both acid and basic wastes, as in plating installations, pH adjustment is performed by proper mixing of streams. Carbon dioxide from flue gas is also used in pH treatment simply by bubbling the gas through an alkaline waste stream. Acetylene sludge (an inpure lime formed in the manufacture of acetylene) is employed as an inexpensive alkali in treating acid wastes, e.g., pickling liquor from a steel mill (Ref. 3).

The neutralization process is subject to the influence of temperature and the resulting heat effects common to most chemical reactions. Generally, in water-based reactions, increasing the temperature of the reactants increases the rate of reaction. In neutralization, the interaction of acid and alkali is frequently exothermic (evolves heat), with an accompanying rise in temperature. An average value for the heat released during the neutralization of dilute solutions of strong acids and bases is 13,360 cal/g. mole of water formed. By controlling the rate of addition of the neutralizing reagent, the heat produced may be dissipated and the temperature increase minimized. For each reaction, the final temperature depends on: the initial reactant temperatures, the chemical species participating in the reaction (and their heats of solution and reaction), the concentrations of the reactants, and the relative quantities of the reactants. In general, concentrated solutions can produce large temperature increases as the relative quantities of the reactants approach stoichiometric proportions. This can result in boiling and splashing of the solution, and accelerated chemical attack on materials. In most cases, proper planning of the neutralization scheme with respect to concentration of neutralizing agent, rate of addition, reaction time, and equipment design can alleviate the heating problem.

3. Output Streams

The products of neutralization can be liquid, solid, gaseous, or a combination. A product's physical form is not related to the form of the reactants, but to its own chemical composition and that of its environment. The chemical species present in the neutralized stream may include the original components of the waste stream, in addition to material from the neutralizing agent. The concentrations of the individual species will depend on the solubility of the products formed during reaction. For example, neutralizing hydrochloric acid with lime yields dissolved calcium chloride as a product remaining in the stream; however, neutralizing sulfuric acid with lime produces solid calcium sulfate as a slurry or sludge, which removes most of the calcium and sulfate from solution. In the case where a solid product is present, further treatment to separate the material will be necessary. Gaseous products can be toxic, as in the case of hydrogen sulfide gas formed during the acid neutralization of a basic stream containing sulfide salts. Provisions must be made for the containment and disposal of hazardous vapors if their formation cannot be avoided.

D. EQUIPMENT AND MATERIALS

The equipment required may be as varied as the reactions that can be classified as neutralizations. A few examples will indicate the range of possibilities: absorption towers to neutralize acid flue gas with aqueous alkali (venturi scrubbers); filter beds of limestone granules (Ref. 4) to neutralize certain acidic liquid wastes; and aeration systems to introduce carbon dioxide into alkaline streams. But the most commonly occurring scheme for neutralization is the addition of a chemical, in either liquid or solid form, directly into a wastewater stream. The required equipment for this form of treatment is simple, i.e., storage and reaction tanks with accessory agitators, and delivery systems. The tanks may be of any shape, round or square, but must be properly baffled to allow adequate mixing and prevent "short-circuiting." Frequently the neutralization is carried out in a series of reactors to provide better control of the final pH. Such a system with three units is shown in Figure 1 (Ref. 5). There are two addition points for neutralizing agent, controlled by pH monitors. Most of the neutralization occurs in the first reactor with adjustment to the final desired pH taking place just before discharge. In large-scale operations the tanks are often built below ground level, and constructed of concrete.

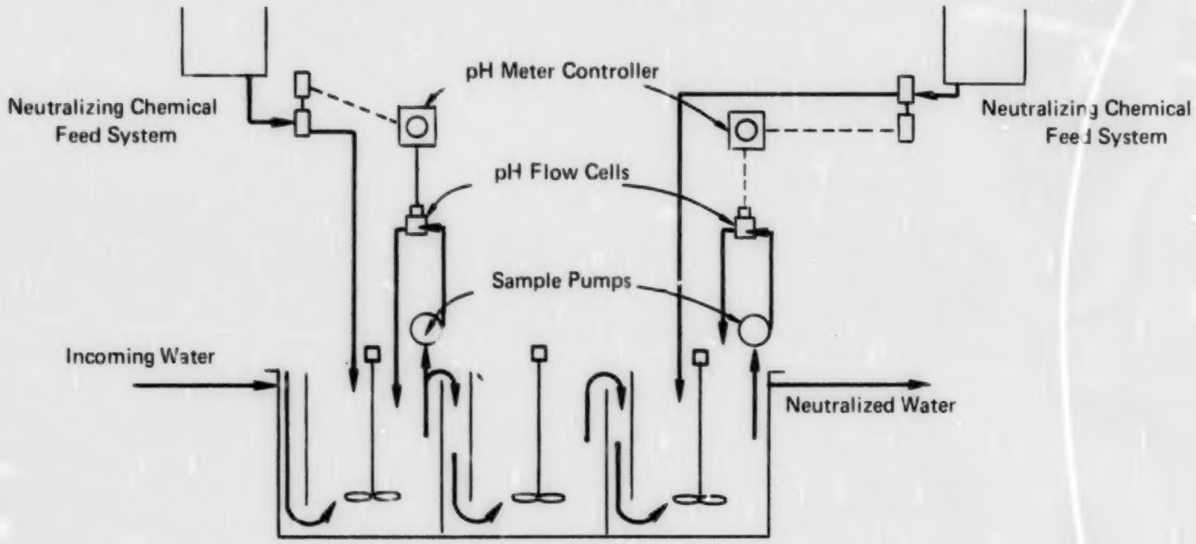

FIGURE 1 CONTINUOUS FLOW NEUTRALIZATION

Appropriate instrumentation must be provided and include pH measurement (and possibly recording) devices with appropriate sample pumps. The feed of neutralizing agent may be regulated automatically by the pH monitoring unit, depending on the requirements of the individual system. There are two common modes of control–feedback, and the more sophisticated, feedforward (Ref. 5). The feedback mode allows a measurable error before

before instituting control. It alters its output until the measured pH and the set point value agree. The result is often undesirable oscillations in the pH of the neutralized mixture. By monitoring the influent stream (by pH measurement or titration), a feedforward controller can take action before deviations in the effluent pH occur, thus preventing excessive fluctuations.

The design of storage facilities depends on the chemical reagents employed in the treatment process (Ref. 2). Caustic solutions and acids may be stored in the open, but quicklime should be kept in waterproof silos, hoppers, or even bags. Delivery systems depend on the physical form of the reagents. Liquids may be transferred with pumps, while slurries can be moved through gravity piping, pumps, or open flumes. Ancillary equipment might include installations such as equalization basins, clarifiers, or vapor removal systems, depending on the specific neutralization scheme.

In dealing with acids and alkalies, appropriate materials of construction are required to provide reasonable service-life for equipment. Corrosion may result in deterioration of a construction material, e.g., lead is attacked by hydrochloric acid. There are several types of corrosion, but for present purposes it need only be stated that corrosion shortens the useful life of equipment. In many cases, the specific concentration of a reagent is important in selecting the correct material used in pumps, pipes, tanks, etc. Examples of materials recommended for handling different acids and alkalies at ambient temperature are (Ref. 5):

Sulfuric acid (75-95%) – lead
(< 10%) – lead or rubber
Hydrocholoric acid (conc. or dilute) – rubber
Sodium hydroxide (conc.) – 316 SS or rubber
(dilute) – 316 SS, rubber, carbon steel, or cast iron
Calcium hydroxide – 316 SS, rubber, or carbon steel

Other less commonly used materials include: glass, metal alloys such as monel, plastics, e.g., PVC, and even wood. The expense of such materials frequently precludes their use except on a small scale or in situations where there is no alternative. It is important to realize that a vessel need not be constructed entirely of one material; it may be lined with lead, rubber, glass, plastic, or other corrosion-resistant materials. Expected length of service, temperature of operation, desired physical strength, liquid flow rate, and mechanical abrasion are some of the other factors to be considered in materials selection.

III. APPLICATIONS TO DATE

A. PRINCIPAL CURRENT APPLICATIONS

Neutralization is a treatment process of demonstrated technical and economic feasibility, in full-scale use in a wide spectrum of industries. A sample list of industries employing this process is presented in Table 1. As can be readily seen, most industries can produce a wide range of pH in their wastewater, depending on specific products and manufacturing processes. The chemical industry alone accounts for the creation of such diverse wastewater products as those from the manufacture of TNT (pH = 2.6) and reclaimed rubber (pH = 11.5). The list is therefore only an indication of the many existing applications of neutralization.

Sample applications for pH treatment of acidic and alkaline wastes are described in the following paragraphs.

- Acid Exhuasts (Ref. 5) – Industrial processes that utilize acids, e.g., sulfuric, nitric, or hydrochloric, frequently have problems with acid mist in the exhaust. Scrubbing with water on packed bed columns produces an acid-free gas, but the spent water must be neutralized. Alkali is usually added automatically to produce a water stream with a pH of 6.5-7.5 which can be discharged or recycled. In similar sytems, flue gas desulfurization units absorb and neutralize sulfur oxides with alkalies such as lime, limestone, dolomite or caustic soda.
- Petrochemical Waste Streams (Ref. 7) – Neutralization is applied to: (1) washwaters, acid or alkaline, (2) spent caustics, (3) acid sludges from alkylation, sulfonation, sulfation, and acid treatments, and (4) spent acid catalysts. Sulfuric acid and carbon dioxide from flue gases are both used to treat spent caustic wastes. Pits filled with lime, limestone, and even oyster shells (a source of calcium carbonate) are utilized to neutralize spent acid sludges.
- Sulfuric Acid Pickle Liquor (Ref. 1) – In small-scale operations (less than 5,000 gpd) neutralization of pickle liquor from steel cleaning operations can be performed in a batch, usually with quicklime. Typically, pickle liquor contains on the order of 70 grams of iron and 170 grams of sulfate per liter (approximately 5% sulfuric acid by weight). Large waste streams can be handled in continuous flow systems (as shown in Figure 1) and other suitable alkaline agents may be employed. If calcium-based materials are utilized in the neutralization, calcium sulfate will form a product sludge, which is usually dewatered by vacuum filtration or placed in a lagoon. The formation of a flocculated ferrous hydroxide precipitate (at neutral pH) can produce a solid with poor settling and filtering properties. Thus an oxidation step is often employed since ferric hydroxide is very insoluble, and there is an optimum ratio of ferric to ferrous ions at which the sludge can be handled most readily.

TABLE 1

INDUSTRIES USING NEUTRALIZATION

INDUSTRY	WASTEWATER pH RANGE
Pulp and Paper	Acidic & Basic
Dairy Products	Acidic & Basic
Textiles	Basic
Pharmaceuticals	Acidic & Basic
Leather Tanning and Finishing	Acidic & Basic
Petroleum Refining	Acidic & Basic
Grain Milling	Acidic & Basic
Fruits and Vegetables	Acidic & Basic
Beverages	Acidic & Basic
Plastic and Synthetic Materials	Acidic & Basic
Steel Pickling	Acidic
By-product Coke	Basic
Metal Finishing	Acidic
Organic Chemicals	Acidic & Basic
Inorganic Chemicals	Acidic & Basic
Fertilizer	Acidic & Basic
Industrial Gas Products	Acidic & Basic
Cement, Lime and Concrete Products	Basic
Electric and Steam Generation	Acidic & Basic
Non-Ferrous Metals—Aluminum	Acidic

Source: Ref. 6

- Hydrochloric Acid Pickle Liquor (Ref. 8) – Although in the past hydrochloric acid was not so widely used as sulfuric acid in steel pickling operations, today there is a trend toward conversion to HCl. Up to 1500 gpm of acid rinse waters, containing up to 0.5g/l free hydrochloric acid and up to 0.87g/l ferrous chloride, are treated. An aeration step is included in the process to oxidize the iron which then precipitates as ferric hydroxide. This precipitate and unreacted limestone are the only solids to be handled since the major product, calcium chloride, is quite soluble. Temperatures above 49°C and a 25% excess of limestone are employed to increase the system's efficiency.
- Limestone Beds (Ref. 1) – Upflow limestone neutralization beds are used at a resin manufacturing plant in New York to treat wastewater containing hydrochloric acid and some sulfuric acid. The unit is capable of operating at flows of up to 13.6 gpm/sq ft with 1% hydrochloric acid. The limestone beds are three feet deep with a cross sectional area of 113 sq ft. Present design would call for substantially deeper beds.
- Metal Finishing Operations (Ref. 1) – A plant manufacturing automobile bumpers in Ohio produces wastewater containing sulfuric, phosphoric, hydrochloric and chromic acids, as well as metal ions. Combined with alkaline

wastes, the final waste stream pH is between 1.5 and 3.0 with a flow rate of about 1000 gpm. Neutralization is carried out in a series of three lead-lined reactors, each of almost 7,500 gal capacity. A slurry of dolomitic lime is added to the first and third reactors, to produce an effluent with a pH of 8.0 to 8.5.

- Plating Wastes – A large plating shop in Massachusetts presents a good example of small-scale neutralizations, both batch and continuous flow. As part of an electrolytic treatment scheme for cyanide rinse waters (about 20,000 gpd) a final pH adjustment is necessary before discharge. This neutralization occurs in a gravity sump equipped with a mixer and pH controller. Either dilute sulfuric acid or dilute caustic soda is added as required to produce a final pH of 6.5–8.5. Also, batch neutralization is practiced on acid and spent chromate dips, and on spent alkalis and floor spills. There is no automatic pH control; the appropriate level is reached by sampling and subsequent addition of the required quantity of acid or alkali.
- Acid Mine Drainage (Refs. 10, 11) – In many underground mines (particularly coal mines) iron pyrite, FeS_2, is oxidized in the presence of air and water to sulfuric acid and ferric sulfate. Treatment of such an acidic stream usually entails various combinations of neutralization, aeration, settling and sludge disposal. Due to the large quantities of wastewate to be treated, selection of a neutralizing reagent is of prime importance if the process is to be economically feasible. Also, one must consider the handling of large quantities of sludge which can be produced during neutralization. Different limes and limestones have been used, with varying amounts of success.

As stated earlier, many neutralizations follow the same theme, addition of a neutralizing reagent to an acidic or basic waste stream. The previous examples have described the types of materials treated and diverse schemes for carrying out the treatment. The list is not meant to be all-inclusive, but to convey the basic similarity of the methods commonly employed.

B. Potential Applications to Waste Treatment

Today, neutralization is widely used for waste treatment, and is technically feasible. However, there are areas in which the process might be employed more effectively. For example, in the treatment of acid mine drainage, only in the recent past has neutralization become economically attractive. Studies were undertaken (Ref. 11) to optimize a process which twenty years ago was throught to be impractical as applied to acid mine drainage. Changing environmental laws, improved equipment design, and revised raw material costs all contributed to promoting the use of neutralization in this case.

Other areas in which work is being conducted involving applications of neutralization include:

- U.S. Bureau of Mines study to define a process for treating electroplating wastes (Ref. 17) – By combining various acid wastes and alkaline cyanide wastes, a neutral pH is obtained. Also, there is almost total precipitation of the cyanide and metals. The treatment is successful in handling wastes with dilute and concentrated levels of cadmium, copper, nickel, and iron. The cost of this simple mixing process is low since a neutralizing reagent is not required.
- Neutralizing wastewater to reduce the lead content to below detectable limits (Ref. 12) – An electronics company in New York is investigating various neutralizing reagents (and combinations thereof) as precipitants for lead. By bringing the pH of a lead in nitric acid waste from 1.6 up to 8.5 with alkalies, a very effective separation of the metal can be obtained.

As can be seen from these examples, the potential applications of neutralization entail an extension and refinement of existing uses. In the future, industries which have previously not been legally required to neutralize wastewater, will find themselves under pressure to do so. But the technology of pH adjustment is well documented and such new applications will be primarily adaptations of present techniques.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

The energy required to operate a neutralization process depends on the actual operations involved and the size of the stream to be treated. In a small-scale operation, the energy requirement would be primarily for electricity to run mixers and pumps. Such would be the case in an electroplating shop, treating 10,000-100,000 gpd of wastewater. An operation in this range might consume up to 100,000 kWh per year in neutralizing its waste streams. However, in other industries such as steel, pickling waste streams can be on the order of millions of gallons per day. Larger mixers and pumps are required, as well as additional pieces of equipment, such as feeders for lime, agitators for clarifiers, etc. In all, such a system could consume well over a million kWh per year. Differences of one or two orders of magnitude would not be unexpected between various pH adjustment schemes. Thus, there is no simple means to predict the energy requirements of a neutralization process until the size of the waste stream and the design of the system are determined.

B. ENVIRONMENTAL IMPACTS

After neutralization a waste stream will usually show an increased total dissolved solids content due to addition of the chemical agent, but there may also be an accompanying reduction in the concentration of heavy metals if the treatment proceeds to alkaline pH's. Conversely, in neutralizations involving the addition of acid to alkali, there is the possibility of solids dissolution. This may, on occasion, be disadvantageous, particularly if the suspended matter is slated for removal, e.g., by filtration. The anions resulting from neutralization of sulfuric and hydrochloric acids are sulfate and chloride, respectively. These ions are not considered hazardous, but there are recommended limits for discharge, based primarily on problems in drinking water. The common cations present after neutralization involving caustic soda and lime (or limestone) are sodium and calcium (possibly magnesium), respectively. These ions are not toxic and there are no recommended limits; however, calcium and magnesium are responsible for water hardness and the accompanying scaling problem. The carbonate produced during limestone neutralization is also harmless both in solution and as carbon dioxide gas.

With regard to atmospheric emissions, one must be cautious not to indiscriminately neutralize wastewater streams. Acidification of streams containing certain salts, such as sulfide will produce toxic gases. If there is no satisfactory alternative, the gas must be removed through scrubbing or some other treatment. In cases where solid products are formed (as in the precipitation of calcium sulfate, or heavy metal hydroxides), clarifier/thickeners and filters must be provided. If the precipitate is of sufficient purity, it would be a salable product; otherwise, a disposal scheme must be devised.

C. ECONOMIC ANALYSIS

The capital investment for neutralization depends on the specific treatment process selected and the size of the stream to be treated. As described in the section on energy requirements, there can be differences in capital costs of orders of magnitude. The following examples will indicate some of the cost differences to be encountered:

- A treatment facility built in 1969 capable of neutralizing 1500 gpm of hydrochloric acid pickle liquor with limestone required a total capital investment of $1,360,000 with an operating cost of approximately $0.24/1000 gal. (Ref. 8).
- A 1971 study of limestone treatment of acid mine drainage (sulfuric acid) estimated that capital costs for treating a stream of about 900 gpm could range from $352,000 to $1,238,000 depending on the composition of the stream. High levels of iron, aluminum, and sulfate contribute to larger capital investment, particularly in the area of sludge handling equipment. For the same reason the estimated cost of operation ranged from $0.35 to $3.76 per 1000 gal (including sludge disposal).

These examples are meant to illustrate the variation in investment and operating costs between different processes, and in the same process operating on different quality wastes. It would be inappropriate to draw conclusions concerning investment capital for neutralization without some knowledge of the system. Materials of construction and the need for sludge-handling equipment are just two additional factors that can drastically alter an economic analysis. With regard to operating costs, similar considerations, such as sludge disposal costs, may be critical. For comparison purposes, prices for disposal of acid or alkali waste quoted recently by waste management facilities were between $60 and $250/1000 gal (Ref. 13).

In the design of a system, the selection of the neutralizing reagent is a decision that must be made not only on chemical, but also, on economic grounds. As an indicator of relative costs for alkaline chemicals (Ref. 1), Table 2 presents a comparison. Note that basicity is expressed in terms of grams of CaO per gram of material. One can readily see that caustic soda is the most expensive alternative. However, because of its reactivity, solubility, and the lack of insoluble reaction products, it is often preferred. By an intelligent choice of neutralizing agent, savings in capital and operating costs can often be realized.

TABLE 2

COSTS OF ALKALINE REAGENTS

	$/ton (Ref. 14)	Basicity Factor	$/ton of Basicity	Relative Cost
Caustic Soda (solid)	290	0.687	422.13	15.89
Quicklime	25	0.941	26.57	1.00
Limestone	19	0.489	38.85	1.46

To provide further guidance in understanding the economics of a neutralization process, a "simulated" sample system is illustrated in Figure 2. This design, along with the description in Table 3, represents a common scheme for lime neutralization of a waste stream containing sulfuric acid. An economic analysis of the treatment process is shown in Table 4. For a 1 mgd (about 700 gpm) stream of 1% sulfuric acid the capital investment is $1,050,000 and the operating cost is $2.65/1000 gal. The capital cost is quite reasonable considering the examples presented earlier in this section. The operating cost (excluding sludge disposal) is also in the range one would expect. It is interesting to note that the cost of lime accounts for over half the total operating cost, while electricity (675,000 kWh) is only about 15%.

Placing an exact price on the sludge disposal is difficult. The chemical composition of the material will influence the choice of disposal method. A sludge containing large quantities of heavy metals may not be suitable for landfill, due to the possibility of leaching, and a more costly method may have to be devised. Conversely, a relatively pure sludge of calcium sulfate might be sold as a byproduct and count as a credit.

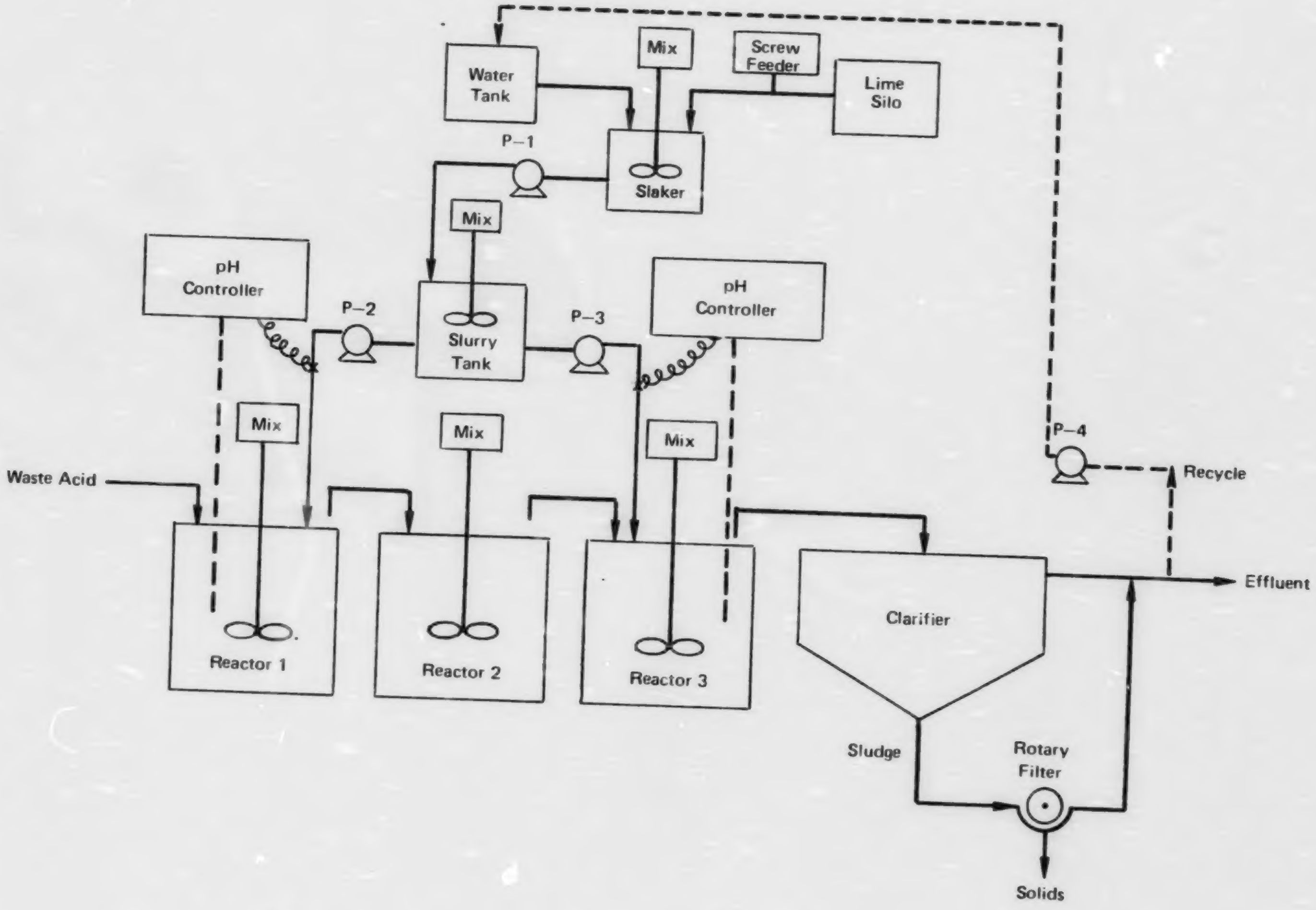
Water Tank
Mix
Screw Feeder
Lime Silo
P–1
Slaker
Mix
pH Controller
P–2
Slurry Tank
P–3
pH Controller
Mix
Mix
Mix
P–4
Waste Acid
Recycle
Reactor 1
Reactor 2
Reactor 3
Clarifier
Effluent
Sludge
Rotary Filter
Solids

FIGURE 2 LIME NEUTRALIZATION OF SULFURIC ACID WASTE

TABLE 3

REQUIREMENTS FOR LIME NEUTRALIZATION OF SULFURIC ACID WASTE STREAM

Basis:	1 mgd; 1% H_2SO_4 (by volume)	
Equipment:	Three Reactors* (with mixers)	7,500 gal. ea.
	Slaking Tank (with mixer)	1,000 gal.
	Lime Slurry Tank (with mixer)	5,000 gal.
	Water Storage Tank	200,000 gal.
	Lime Silo	2,000 ft.^{3}
	Clarifier	250,000 gal.
	Rotary Filter	11,250 lb/hr. dry solids (Filter cake 50-60% solids)
	Lime Screw Feeder	3,700 lb/hr.
	Pumps	
	P-1	70 gpm
	P-2	70 gpm
	P-3	35 gpm
	P-4	70 gpm
	Two pH Recorder /Controllers (with sample pumps)	
Chemicals:	Quicklime	44 tpd
Utilities:	Electricity (annual basis)	675,000 kWh
Labor:	32 man-hours/day	

*Due to possible acidic conditions, reactors should be lead or rubber-lined. Agitator shafts and blades should be rubber-coated.

TABLE 4

ESTIMATED COST FOR NEUTRALIZATION

Basis: 1 mgd of 1% H_2SO_4 Waste Stream 350 day/year operation

Estimated Capital Investment: $1,050,000

	Annual Quantity	Cost Per Unit Quantity	Annual Cost ($)
Variable Costs			
Operating Labor (Incl. Supv. & Overhead)	11,200 M.H.	$12 M.H.	$135,000
Lime	15,400 tons	$35.00/ton	$539,000
Electricity	675,000 kWh	$ 0.02/kWh	$ 13,500
Maintenance			$ 42,000
Coagulant Aids	3,000	$ 2.00/lb	$ 6,000
Total Variable Costs			$735,500
Fixed Costs			
Taxes and Insurance (2% of Inv.)			$ 21,000
Capital Recovery (10 yrs @ 10%)			$170,500
Total Fixed Costs			$191,500
Total Costs			$927,000
Unit Costs – $/$10^3$ gallons			$ 2.65

NOTE: No costs have been included for sludge disposal or, conversely, credits for gypsum if the latter is saleable.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Neutralization is an accepted part of waste treatment technology; the knowledge required for design, construction, and operation are readily available. The process can handle a wide range of physical and chemical forms. There are numerous possibilities as to the type of neutralization system that can be employed, whether it be limestone beds or addition of liquid caustic soda. Neutralization can be carried out in batch or continuous flow, and the reaction time is usually short so that long retention periods are not required.

Any technical developments which reduce the volume of sludge, and increase its filterability and settleability, whether by chemical or mechanical means, will improve the acceptability of neutralization–from an economic and environmental standpoint. New corrosion resistant materials which could substantially increase the service life of equipment would also introduce significant cost savings. In many cases, research into the process chemistry could be very cost effective. For example, laboratory determination of the correct reagent and concentration to be used in a particular neutralization could cut expenses with respect to raw material costs and equipment costs (by the elimination of over-design).

In conclusion, neutralization is a treatment process of demonstrated technical and economic feasibility. The expertise is available for solving most problems involving pH control. It is recommended that this process be included in all waste treatment facilities and that the system design be carefully selected, with an eye to optimizing both the total capital investment and the operating cost.

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B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD

COMPANY	CONTACT	COMMENTS
Silresim Chemical Corp. Lowell, MA	Dr. John Miserlis, President	Silresim is a waste management facility practicing neutralization on a small scale on waste streams which do not meet effluent guidelines.
New England Plating Co., Inc. Worcester, MA	Bruce Warner, President	N.E. Plating is a large shop with various streams which must be neutralized before disposal.
Armco Steel Corp. Middletown, O	None	Armco has a full scale limestone treatment facility for hydrocholoric acid pickle liquor.
Bituminous Coal Research, Inc.	None	BCR has completed a technical and economic study of limestone treatment of acid mine drainage.
Hooker Niagara Falls, N.Y.	None	Hooker scrubs HCl from waste gas and neutrals in a limestone lagoon.
Chem-Trol Model City, N.Y.	None	Operates centrifugal neutralizer.

OXIDATION, CHEMICAL

Prepared by

Nancy J. Cunningham

I. CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

- Chemical oxidation can detoxify certain hazardous wastes.
- Technology for large-scale application of chemical oxidation is well developed.
- Application to industrial wastes is well developed for cyanides and for other hazardous species in dilute waste streams (phenols, organic sulfur compounds, etc.)
- Laboratory and pilot studies have demonstrated potential for oxidation treatment of other hazardous species including chlorinated hydrocarbons and pesticides in dilute streams.
- Introduction of additional ions into the waste from the oxidizing agent itself is of concern.
- The major cost of oxidation treatment is for the oxidizing chemicals. The economics vary from one waste to another.
- The equipment required is relatively simple, requiring only storage, metering, mixing, pumping, and instrumentation.

B. RECOMMENDATIONS

- We recommend that chemical oxidation be considered for dilute aqueous streams containing the wastes discussed in this report.
- Chemical oxidation should be considred as a first treatment step when the waste contains cyanide.
- Chemical oxidation should be evaluated as a first treatment for wastes that have constituents or concentrations of constituents that are not amenable to other treatment methods.
- Chemical oxidation should be considered as a final polishing step for residual traces of contaminants remaining after certain other treatments.
- A more exhaustive study should be made of the potential for treatment of hazardous species of current concern. Most of the literature deals only with very dilute wastes or with the preparation of materials from basic raw materials via chemical oxidative techniques, and little has been published that is directly relevant to the treatment of concentrated hazardous wastes.

II. PROCESS DESCRIPTION

A. BACKGROUND

The processes discussed here are based on chemical oxidation as differentiated from thermal, electrolytic, and biological oxidation. Ozonolysis, a commonly used chemical method of oxidation for waste treatment and another oxidation process, chlorinolysis, are discussed elsewhere in this report. While oxidation using air or oxygen in solution can be used for waste treatment on sulfites, sulfides and ferrous iron, these oxidations typically are catalyzed with small amounts of materials such as cobalt to increase the reaction rate. Therefore, these catalyzed reactions are discussed elsewhere under Catalysis. Also, the oxidation reactions discussed here should be distinguished from the higher temperature, and typically pressurized, wet oxidation processes, such as the Zimpro process, which are not included in this study.

B. UNDERLYING PRINCIPLES

Oxidation-reduction, or "redox" reactions are those in which the oxidation state of at least one reactant is raised while that of another is lowered. In reaction (1) in alkaline solution:

$$(1)\quad 2MnO_4^- + CN^- + 2OH^- \rightleftharpoons 2MnO_4^{2-} + CNO^- + H_2O$$

the oxidation state of the cyanide ion is raised from -1 to +1 (the cyanide is oxidized as it combines with an atom of oxygen to form cyanate); the oxidation state of the permanganate decreases from -1 to -2 (permanganate is reduced to manganate). This change in oxidation state implies that an electron was transferred from the cyanide ion to the permanganate. The increase in the positive valence (or decrease in the negative valence) with oxidation takes place simultaneously with reduction in chemically equivalent ratios.

Fluorine is a powerful oxidizing agent. The other halogens, including chlorine, are also good oxidizing agents. The positive ions of noble metals are good oxidizing agents. Many of the oxygenated ions, such as BrO_3^- and NO_3^- are strong oxidizing agents in acid solution.

There are, then, many oxidizing agents; however, only a few are convenient to use. The ones that are more commonly used in waste treatment appear in Table 1.

Oxidizing agents vary in strength as illustrated by the following half-reactions arranged in order of decreasing oxidation potentials (i.e., tendency to pick up electrons):

TABLE 1

WASTE TREATMENT APPLICATIONS OF OXIDATION IDENTIFIED

Oxidant	Waste		References
Ozone*	--		
Air (atmospheric oxygen)	Sulfites ($SO_3^{=}$)		
	Sulfides ($S^{=}$)		23
	Ferrous iron (Fe^{++}) – very slow		
Chlorine gas	Sulfide		
	Mercaptans		
Chlorine gas and caustic**	Cyanide (CN^{-})		26
Chlorine dioxide	Cyanide		
	Diquat	pesticides	19
	Paraquat		19
Sodium hypochlorite	Cyanide		6,7,8
	Lead		40
Calcium hypochlorite	Cyanide		6,7,8
Potassium permanganate	Cyanide – organic odors		
	Lead		40
Trace quantities only	Phenol		1,36
	Diquat	pesticides	19
	Paraquat		19
	Organic sulfur compounds		36
	Rotenone		
	Formaldehyde		1,36
Permanganate	Manganese		30
Hydrogen peroxide	Phenol		
	Cyanide		24,35
	Sulfur compounds		9,35
	Lead		40
Nitrous acid	Benzidene		

*discussed in another chapter of this report.

**alkaline chlorination.

Half-reaction	Oxidation Potential (E_0), Volts
$F_2 + 2H^+ + 2e^- \rightarrow 2HF\ (aq.)$	3.06
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.77
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.695
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.359
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33
$2H^+ + 2e^- \rightarrow H_2$	0

Some oxidations proceed readily to CO_2. In other cases the oxidation is not carried as far perhaps because of the dosage of the oxidant, the pH of the reaction medium, the oxidation potential of the oxidant, or the formation of stable intermediates. The primary function performed by oxidation in the treatment of hazardous wastes is essentially detoxification. For instance, oxidants are used to convert cyanide to the less toxic cyanate or completely to carbon dioxide and nitrogen. The oxidant itself is reduced. For example, in the potassium permanganate treatment of phenolics, the permanganate is reduced to manganese dioxide. A secondary function is to assure complete precipitation, as in the oxidation of Fe^{++} to Fe^{+++} and similar reactions.

Table 2 lists the more common oxidation reactions for cyanide treatment and their reaction products. Oxidation reactions for other wastes appear throughout the text.

C. OPERATING CHARACTERISTICS

1. Stream Characteristics

Liquids are the primary waste form treatable by chemical oxidation. The most powerful oxidants are relatively non-selective; therefore, any easily oxidizable material in the waste stream will be treated. If for instance an easily oxidizable organic solvent were used, little of the chemical effect of the oxidizing agent could be used on the hazardous constituent. This, therefore, essentially limits the use of the most commonly used oxidants to aqueous wastes.

Gases have been treated by scrubbing with oxidizing solutions for the destruction of odorous substances, such as certain amines and sulfur compounds. Potassium permanganate, for instance, has been used in certain chemical processes, in the manufacture of kraft paper and in the rendering industry. Oxidizing solutions are also used for small-scale disposal of certain reactive gases in laboratories (Ref. 15).

Oxidation has limited application to slurries, tars, and sludges. Because other components of the sludge, as well as the material to be oxidized, may be attacked indiscriminately by oxidizing agents, careful control of the treatment via multi-staging of the reaction, careful control of pH, etc. are required.

The chlor-alkali industry is reported to use chemical oxidative techniques to remove mercury from ores as well as from the cell-wastes. Mercury removal rates of over 99% are claimed for concentrated ores, and residual mercury levels of less than 0.1 ppm for chlor-alkali sludge.

TABLE 2

CONVENTIONAL WASTE TREATMENT OXIDATION REACTIONS

- Cyanide destruction –– using chlorine gas

(1)	$2NaCN$	$+ 5Cl_2$	$+ 12NaOH \rightarrow$	N_2	$+ 2Na_2CO_3$	$+ 10NaCl$	$+ 6H_2O$
	sodium cyanide	chlorine	sodium hydroxide	Nitrogen	sodium carbonate	sodium chloride	water

- Cyanide destruction –– using hypochlorites

(2)	$2NaCN$	$+ 5NaOCl$	$+ H_2O \rightarrow$	N_2	$+ 2NaHCO_3$	$+ 5NaCl$
		sodium hypochlorite			sodium bicarbonate	

(3)	$4NaCN$	$+ 5Ca(OCl)_2$	$+ 2H_2O \rightarrow$	$2N_2$	$+ 2Ca(HCO_3)_2$	$+ 3CaCl_2$	$+ 4NaCl$
		calcium hypochlorite			calcium bicarbonate		

- Conversion of cyanide to cyanate –– using permanganate

(4)	$2NaCN$	$+ 2KMnO_4$	$+ KOH \rightarrow$	$2K_2MnO_4$	$+ NaCNO$	$+ H_2O$
		potassium permanganate				

- Conversion of cyanide to cyanate –– using chlorine gas

(5)	$NaCN$	$+ Cl_2$	$+ 2NaOH \rightarrow$	$NaCNO$	$+ 2NaCl$	$+ H_2O$
				sodium cyanate		

- Conversion of cyanide to cyanate –– using hypochlorites

(6)	$NaCN$	$+ NaOCl \rightarrow$	$NaCNO$	$+ NaCl$
		sodium hypochlorite	sodium cyanate	

- Conversion of cyanide to cyanate –– using hydrogen peroxide

(7)	$NaCN$	$+ H_2O_2 \rightarrow$	$NaCNO$	$+ H_2O$
		hydrogen peroxide	sodium cyanate	

However, the Pacific Northwest Environmental Research Laboratory, Corvallis, Oregon has reported that it could not duplicate these results on a laboratory scale, perhaps simply because of the variability of the sludges. In a study which recommended the use of sulfide precipitation to remove the mercury (Ref. 28), they tested the use of sodium hypochlorite and chlorine as accessory reagents. Their intent was to oxidatively convert the elemental mercury and insoluble mercurous compounds in the brine sludge to a stable soluble mercuric complex as follows:

$$Hg + ClO^{-} + 3\,Cl^{-} + H_2O \rightleftarrows HgCl_4^{=} + 2OH^{-}$$

other reactions include:

$$2Hg^{+} + ClO^{-} + 7Cl^{-} + H_2O \rightleftarrows 2HgCl_4^{=} + 2OH^{-}$$

$$Hg^{++} + 4Cl^{-} \rightleftarrows HgCl_4^{=}$$

The results indicated that the hypochlorite dissolved nearly as much of the sludge solids as the mercury. Other kinds of treatment would be required to remove the remaining mercury from the residue.

Work has been done on using sodium hypochlorite for leaching mercury from low grade ores. Residual mercury was present, which suggests that the reaction may be incomplete. The extent to which this technique could be extended to the treatment of industrial wastes may be limited because of the inefficiency of use of the oxidant and the incompleteness of removal of mercury from sludge solids.

Powders and other solids would usually be put into solution prior to the use of chemical oxidation. However, as with many chemical reactions,like neutralization of acids with limestone, reactions may be possible that depend upon a reaction between a liquid and solid phase.

Chemical oxidation can be used to treat both organic and inorganic waste components. Since some oxidizing agents may react violently in the presence of significant quantities of readily oxidizable organic material, either the organic matter or the oxidizing agent should be added in small quantities, so that large momentary excesses are avoided. Widely varying concentrations of non-oxidizable ions of heavy metals are well tolerated. In fact, the primary use of chemical oxidation for waste treatment is in the conversion and destruction of cyanides from plating operations where metals, such as zinc, copper and chromium, are present.

2. How Process Operates

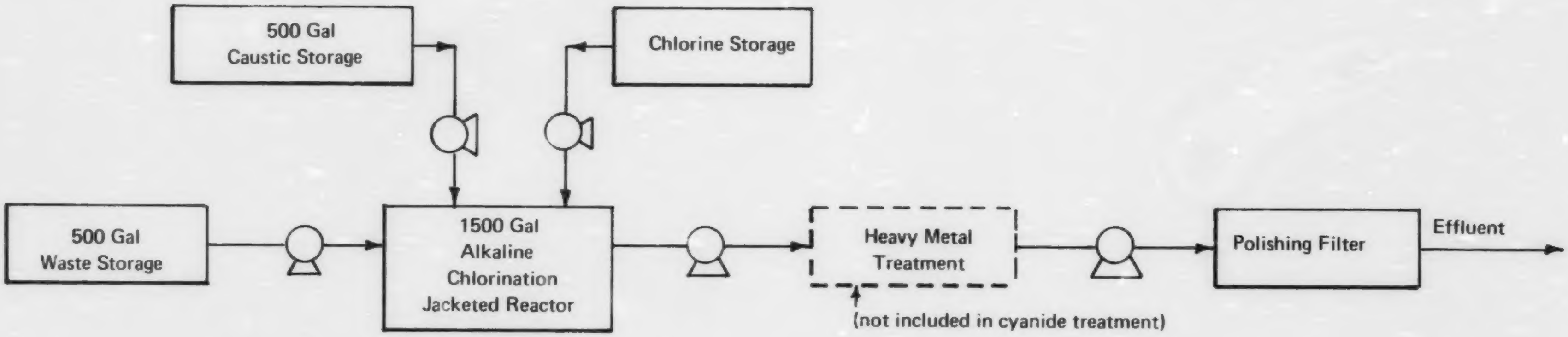
The first step of the chemical oxidation process is the adjustment of the pH of the solution to be treated. In the use of chlorine gas to treat cyanides, for instance, this adjustment is required because acid pH has the effect of producing hydrogen cyanide and/or cyanogen chloride, both of which are poisonous gases. The pH adjustment is done with an appropriate alkali; sodium hydroxide, for example. This is followed by the addition of the oxidizing agent. Mixing is provided to contact the oxidizing agent and the waste. Because some heat is often liberated, more concentrated solutions will require cooling. The agent can be in the form of a gas (chlorine gas) or as a solution (hydrogen peroxide) or perhaps as a solid if there is adequate mixing. Reaction times vary but are in the order of seconds and minutes for most of the commercial-scale installations. Additional time is allowed to ensure complete mixing and oxidation. At this point, additional oxidation may be desired and, as with cyanide destruction, often requires the readjustment of the pH followed by the addition of more oxidant. Once reacted, this final oxidized solution is then generally subjected to some form of treatment to settle or precipitate any insoluble oxidized material, metals, and other residues. A treatment for the removal of what remains of the oxidizing agent (both reacted and unreacted) may be required. A product of potassium permanganate oxidation is manganese dioxide (MnO_2) which is insoluble and can be settled or filtered for removal.

3. Output Stream

While some stream components may be added or removed, the output stream from chemical oxidation is very similar to the input stream. Oxidizing agents such as potassium permanganate and potassium dichromate introduced to the reaction mixture ions that are not easily separable from the product streams. Oxidizing agents such as oxygen and hydrogen peroxide have the advantage that they introduce no such foreign ions to the reaction mixture. Oxidizing agents often have a reaction product, such as MnO_2, that is insoluble and can be removed by filtration.

D. EQUIPMENT AND MATERIALS

Only very simple equipment is required for chemical oxidation. This includes storage vessels for the oxidizing agents and perhaps for the wastes, metering equipment for both streams, and contact vessels with agitators to provide suitable contact of oxidant and waste. Some instrumentation is required to determine the concentration and pH of the water and the degree of completion of the oxidation reaction. The oxidation process may be monitored by an oxidation-reduction potential (ORP) electrode. This electrode is generally a piece of noble metal (often platinum) which is exposed to the reaction medium, and which produces an EMF output that is empirically related to the reaction condition by revealing the ratio of the oxidized to the reduced constituents. Figure 1 shows a process flow diagram for a typical chemical oxidation system.


500 Gal
Caustic Storage
Chlorine Storage
500 Gal
Waste Storage
1500 Gal
Alkaline
Chlorination
Jacketed Reactor
Heavy Metal
Treatment
(not included in cyanide treatment)
Polishing Filter
Effluent

Treatment: Batch
Waste: Concentrated Cyanide Waste
7000 ppm Copper Cyanide
1000 ppm Sodium Cyanide
Waste Processing Capacity: 1000 Gal/Day
Operating Period: 240 Days/Yr
8 Hours/Day

Utilities Summary:
1500 Gal/Day Cooling Water
Raw Materials:
95 lbs/Day NaOh
227 lbs/Day Chlorine

FIGURE 1 EXAMPLE PROCESS FLOWSHEET – OXIDATION

Calgon, DuPont, and Oxymetal Industries are among numerous companies that have commercial units for the removal of cyanides from industrial effluents. Calgon uses cupric ions to catalyze cyanide oxidation. Chemical costs are estimated at 85-90¢/lb of cyanide destroyed. DuPont uses Kastone (41% H_2O_2 and formaldehyde) to convert cyanide to cyanate. Oxymetal Industries has a package unit which oxidizes five pounds sodium cyanate per hour (Ref. 34). All of these units offer the user a pre-engineered system for a specific waste or range of wastes.

The chemical oxidants that have been identified in this study are commercially available. Their prices are as follows *(OPD Marketing Reporter,* April 1976):

Potassium permanganate	52¢/lb in 350-lb barrels
Chlorine gas	6.3¢/lb in ton containers
Calcium hypochlorite	47¢/lb
Sodium hypochlorite	58¢/lb
Hydrogen peroxide, 35% solution –	15.5¢/lb
Chromic acid (CrO_3)	58¢/lb

Since varying amounts of these chemicals are required for treatment of specific wastes, it is not possible to say that the least expensive oxidizing agent on a weight basis would lead to the least expensive overall treatment system. The characteristics of a number of common oxidizing agents are described in the following paragraphs.

1. Potassium Permanganate ($KMnO_4$)

Potassium permanganate has been used for destruction of organic residues in wastewater and in potable water. Its usual reduced form, manganese dioxide (MnO_2), can be removed by filtration. $KMnO_4$ reacts with aldehydes, mercaptans, phenols, and unsaturated acids. It is considered a relatively powerful oxidizing agent.

2. Hydrogen Peroxide (H_2O_2)

Hydrogen peroxide has been used for the separation of metal ions by selective oxidation. In this way it helps remove iron from combined streams by oxidizing the ferrous ion to ferric which is then precipitated by the addition of the appropriate base. In dilute solution ($< 30\%$) the decomposition of hydrogen peroxide is accelerated by the presence of metal ion contaminants. At higher concentrations of hydrogen peroxide, these contaminants can catalyze its violent decomposition. Hydrogen peroxides should be added slowly to the solution with good mixing. This caution relates to other oxidants as well. If the follow-on treatment involves distillation or crystallization, the absence of all unspent peroxides must be confirmed since these techniques tend to concentrate the unused reagent. Hydrogen peroxide has also been used as an "anti-chlor" to remove residual chlorine following chlorination treatment.

U)

3. Chromic Acid (CrO_3)

Chromium trioxide, CrO_3, is commercially called chromic acid. It is used as an oxidizing agent in the preparation of organic compounds. It is often regenerated afterward by electrolytic oxidation. In the oxidation of organic compounds, chromic acid in a solution of sulfuric acid is reduced and forms chromium sulfate ($Cr_2(SO_4)_3$).

III. APPLICATIONS TO DATE

A. HISTORY OF USE

Oxidation reactions are among the most common of chemical reactions. The experience with these reactions for waste treatment is primarily related to removal of trace contaminants in water effluents and for cyanide treatment from operations such as plating and metal finishing. The former are of interest only as they identify potential oxidants and type of materials that can be oxidized. The latter, while often relating to dilute cyanide rinse wastes, can be extended to more concentrated solutions which have relevance to this contract. Also, one company we visited reported that soluble solid cyanide wastes were treated by first putting them into solution with water and then slowly metering them into the more dilute cyanide waste for treatment.

B. PRINCIPAL CURRENT APPLICATIONS TO INDUSTRIAL WASTE

The following paragraphs describe some selected examples of the application of chemical oxidation to hazardous waste management problems.

1. Oxidation of Cyanide Effluents

Numerous plating and metal finishing plants use chemical oxidation methods to treat their cyanide wastes. Cyanides and heavy metals are often present together in plating industry wastes. Their concentration and their value influence the selection of the treatment process. If the cyanide and heavy metal are not economically recoverable by a method such as ion exchange, the cyanide radical is converted either to the less toxic cyanate or to CO_2 and N_2 by oxidation, while the heavy metal is precipitated and removed as a sludge.

Chemical oxidation is applicable to both concentrated and dilute waste streams, but the competing processes are more numerous for the concentrated streams. These methods include thermal and catalytic decomposition of the cyanide and decomposition using acidification.

In treating cyanide waste by oxidation, hypochlorite or caustic plus chlorine (alkaline chlorination) may be used to oxidize the cyanide to cyanate or to oxidize it completely to nitrogen and carbon dioxide. It is a fast reaction which is adaptable to either batch or continuous operation. Smaller volumes would be treated in a batch system for simplicity and safety. Figure 2 describes a batch process to destroy cyanide.

The destruction is believed to proceed according to the following equations:

$$(1)\quad NaCN + Cl_2 \rightarrow CNCl + NaCl$$

$$(2)\quad CNCl + 2NaOH \rightarrow NaCNO + NaCl + H_2O$$

$$(3)\quad 2NaCNO + 4NaOH + 3Cl_2 \rightarrow 6NaCl + 2CO_2 + N_2 + 2H_2O$$

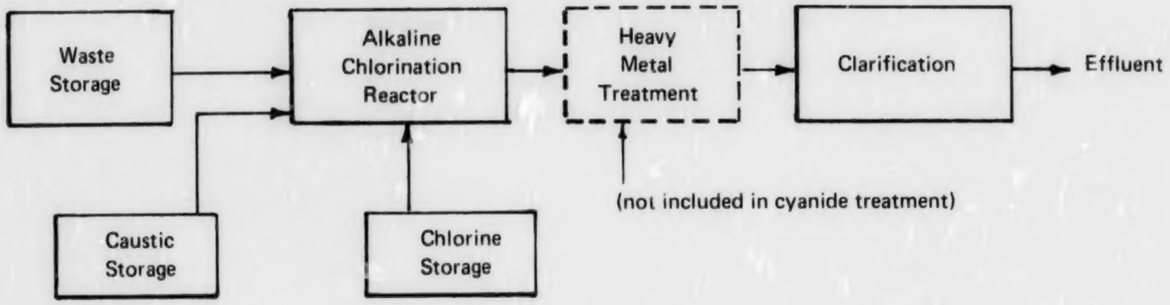


FIGURE 2 CYANIDE WASTE TREATMENT USING ALKALINE CHLORINATION

The rate of the second reaction is dependent upon pH and proceeds rapidly at a pH of 11 or higher. About 8 parts chlorine and 7.3 parts sodium hydroxide are required per part of cyanide. Neutralization is required after treatment because the waste is generally alkaline.

Calcium, magnesium, and sodium hypochlorite are frequently used in place of gaseous chlorine even though the chlorine is more rapid and costs about half as much as the hypochlorites. This is because they are easier and safer to use and do not require the addition of supplementary alkali. Calcium hypochlorite will give more sludge than the sodium hypochlorite if certain anions such as sulfate are present.

There are problems associated with alkaline chlorination of cyanide if soluble iron or certain other transition metal ions are present. The iron forms very stable ferrocyanide complexes which prevent the cyanide from being oxidized.

Potassium permanganate and hydrogen peroxide are also used to oxidize cyanide wastes.

Potassium permanganate ($KMnO_4$) is not used widely for the destruction of cyanide. However, Reference 8 states that oxidation by permanganate is a method of cyanide removal which has been reduced to commercial practice. One advantage of the use of permanganate is that there is no need to monitor pH. Once the pH adjustment has been made there is continuous formation of the hydroxide ion

$$KMnO_4 + 3CN^- + H_2O \rightarrow 3CNO^- + 2MnO_2 + 2OH^-$$

to constantly keep the reaction medium on the alkaline side. This is fortunate because otherwise there is the danger that if the pH drops to between 6 and 9, hydrogen cyanide and/or cyanogen, both of which are poisonous gases, may be formed. With other oxidative methods the reaction medium is kept alkaline by the addition of alkali.

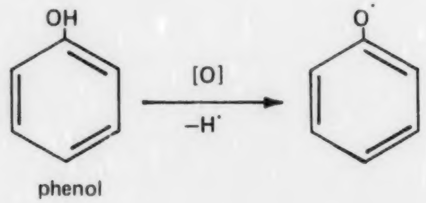
The use of permanganate oxidizes the waste cyanide only to the cyanate. Simple acid hydrolysis can be used to further treat the cyanate, converting it to CO_2 and N_2.

Potassium permanganate is a powerful oxidizing agent. Since it is relatively expensive (40-50¢/lb), it may not have received widespread use because there are other less expensive oxidants available. A small plater could find application for this material, however, because there would be little need for instrumentation or testing to monitor the reaction and there would not be the requirement of a large capital investment.

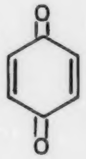
Lawes and Mathre (Ref. 24) describe a process which uses a combination of hydrogen peroxide (H_2O_2) and formaldehyde with the addition of a magnesium salt for the detoxification of cyanide wastes. The temperature and pH are important variables in this reaction. The preferred reaction temperature is 10 – 82°C and the pH of the waste should be in the range of 9 to 12.5. The waste treatment was designed specifically for treatment of wastewaters from zinc plating operations. When the rinse waters are treated, the settled or filtered basic zinc salts can be recycled to the zinc electroplating step. Previously, peroxygen compounds could not be effectively and economically used for cyanide destruction without the use of a catalyst. A catalyst that is often used is a metal ion such as Cu^{++}. Indeed, Cu^{++} is often found in plating solutions. However, it is a pollutant which must eventually be removed. Also, because of the decomposition of the hydrogen peroxide that occurs in dilute aqueous solutions ($< 30\%$) which is accelerated by the presence of metal ion contaminants, addition of a metal ion to catalyze the reaction may make the reaction less efficient. It should be noted that while metal ions cause decomposition in dilute solutions they may actually catalyze violent decomposition in higher concentration solutions of hydrogen peroxide (70-90%) even though present in only trace amounts. This type of reaction of powerful oxidants is not uncommon. Therefore these properties of oxidants should be considered when thinking of treating the more concentrated wastes such as those normally incinerated or disposed of on land.

2. Oxidation of Phenol

Oxidation reactions involving phenol are often complex, since the reaction products depend upon the substituents. The reactions are believed to involve as a first step the removal of the hydroxyl hydrogen to yield a phenoxy radical:



The eventual reaction products can include quinone which is considered more toxic than phenol. In one commercial reaction, for instance, the oxidation of phenol with chromic acid is designed to yield quinone:



Spicher and Skrinde (Ref. 42) propose that the reaction mechanism involves first the production of the quinone and then the rupture of the ring followed by the oxidation of the ring fragments if sufficient oxidant is present. The reaction does not usually go quite as far as Spicher and Skrinde suggest in their proposed reaction using potassium permanganate:

$$3C_6H_5(OH) + 28KMnO_4 + 5H_2O \rightarrow 18CO_2 + 28KOH + 28MnO_2$$

although the reaction usually does go to the stage of opening the ring.

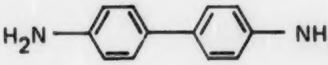
Chemical oxidation of phenols has found application to date only on dilute waste streams. Potassium permanganate is one of the oxidants that is used. It is reported to be added and then some further time is allowed for the phenol to be oxidized to carbon dioxide and water (Ref. 1). The potassium permanganate is reduced to manganese dioxide (MnO_2) which is a filterable solid. In one application the product MnO_2 has been found to act also as a coagulant aid to settle other material from the waste stream. Because of the high potential for formation of chlorophenols, chlorine gas is not frequently used.

When phenol is present only in trace quantities, the economics appear favorable for chemical oxidation. It has been used in the treatment of potable water. Removal of 1 ppm phenol in this application can be accomplished by the addition of 6 to 7 ppm potassium permanganate (Ref. 36).

3. Oxidation of Other Organics

Chemical oxidizing agents have been used for the control of organic residues in wastewaters and in potable water treatment. Among the organics for which oxidative treatment has been reported are: aldehydes, mercaptans, phenols, benzidine, and unsaturated acids. For these applications sodium hypochlorite, calcium hypochlorite, potassium permanganate and hydrogen peroxide have been reported as oxidants. In one application nitrous acid was used.

Benzidine, an organic used in the manufacture of dyes, is considered a carcinogen. Its concentration is generally reduced to ppb in wastewaters prior to discharge for this reason. Nitrous acid oxidation is used to achieve this effluent quality. While biodegradation, carbon adsorption, radiation, and oxidation by ozone and oxidation by other chemicals such as hydrogen peroxide has been suggested, only the oxidation (commonly called diazotization) using nitrous has been used on a full scale basis (Ref. 21). The reaction of benzidine



with an excess amount of nitrous acid in a strong acid reaction medium yields the quinone form, 4,4′-dihydroxybiphenyl and/or similar products. The reaction products cannot revert back to benzidine. The quinone product is toxic also but considered less so than the reactant, benzidine. Since the effluent stream is very dilute, no secondary treatment is required.

The reaction of formaldehyde with potassium permanganate in neutral or mildly alkaline solutions is as follows:

$$3HCHO + 4KMnO_4 \rightarrow H_2O + 3CO_2 + 4KOH + 4\ MnO_2$$

The reaction is the basis for a simple gas washing apparatus in the textile industry where permanent-press fabrics are processed.

Because strong oxidant (such as *potassium permanganate*) may be decomposed by alcohols and some other organic solvents, as well as acting as oxidants for them, it is anticipated that their use on concentrated organic wastes will not be cost-effective. This does not rule out the possibility that some types of organic waste might be converted on a commercial scale to useable products via oxidation reactions similar to those used in the organic chemicals industry. However, it does not appear that the wastes being investigated are susceptible to this form of treatment.

4. Oxidation of Sulfur Compounds

Much of the work on oxidative treatment of sulfur compounds is centered on the problem of odor removal. Scrubbers using oxidizing solutions of potassium permanganate, for example, have been used to remove organic sulfur compounds from air. Thiophene is one of these compounds, in which the molecule is unsaturated and is susceptible to complete degradation.

$$26MnO_4 + 3C_4H_4S + 4H_2O \rightarrow 26MnO_2 + 12CO_2 + 3SO_4^{=} + 20\ OH^-$$

Chlorine and calcium hypochlorite have been used to prevent accumulation of soluble sulfides in sewer lines (Ref. 9). If an excess of chlorine is added to a wastewater containing sulfide, the sulfide will be oxidized to sulfate.

$$HS^- + 4Cl_2 + 4H_2O \rightarrow SO_4^= + 9H^+ + 8Cl^-$$

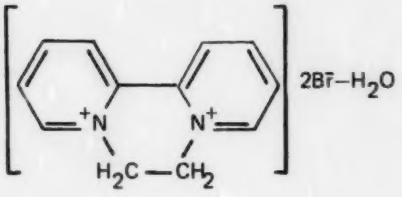
On a pure waste stream containing only small concentrations of sulfide, the chlorine requirement would be nearly 9 parts (by weight) for each part of sulfide. In streams where there are other oxidizable constituents, this requirement may actually be in the order of 15 to 20 parts.

Hydrogen peroxide has also been used for this application of sulfide oxidation. In a wastewater which contained about 6 mg/l total sulfide, the addition of 30 mg/l hydrogen peroxide (H_2O_2) reduced the concentration of sulfide to less than 1 mg/l. The average retention time was about two hours (Ref. 9).

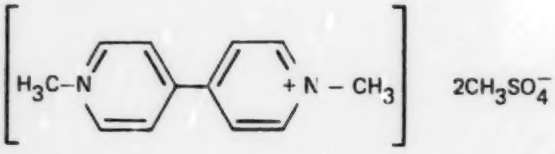
Although later developed into a catalyzed, two-stage, higher temperature system, the initial concept of the Sulfox® system for control of sulfur emissions was to convert hydrogen sulfide to elemental sulfur by oxidation with atmospheric oxygen (Ref. 23). Knowing that there was a strong tendency for sulfide reactions to go to the thiosulfate and sulfite stages, attempts were made to find the kind of solutions which could regulate the extent of the oxidation. Caustic solutions were not favorable. It turned out that ammoniacal solutions gave improved selectivity. The availability of by-product ammonia at refineries that had sulfur emission problems made the use of ammoniacal solutions appear promising. Later improvements to the system involved the use of a cobalt catalyst.

5. Oxidation of Pesticides

Because of the resistance of pesticides to biodegradation, chemical oxidative methods have been investigated to remove pesticide residues from water. Gomaa and Faust (Ref. 19) experimented with potassium permanganate, chlorine, and chlorine dioxide to remove residual Diquat and Paraquat from water.



Diquat



Paraquat

With potassium permanganate oxidation, manganese dioxide was precipitated as expected. The application of $KMnO_4$ at a molar concentration 25 times that of the two pesticides causes fairly complete oxidation to oxalate, ammonia and water. The reaction is said to go through several intermediate reactions and that the reaction rates are pH dependent being faster above pH 8. In an alkaline medium

$$3(C_{12}H_{12}N_2)^{2+} + 40MnO_4^- + 2OH^- \rightleftharpoons 40MnO_2 + 18C_2O_4^= + 6NH_3 + 10H_2O$$

Diquat

$$(C_{12}H_{14}N_2)^{2+} + 14MnO_4^- \rightleftharpoons 14MnO_2 + 6C_2O_4^= + 2NH_3 + 4H_2O$$

Paraquat

When using chlorine dioxide as the oxidizing agent on these substances in concentrations of 15 and 30 mg/l, the reactions were complete in less than one minute. These rates were observed at pH values above 8. At pH 9.04, for example, 15 mg/l of Diquat treated with 6.75 mg/l chlorine dioxide had a residual Diquat of 0.00 and a residual chlorine dioxide of 2.61.

6. Oxidation of Lead

Although for a particular application other methods were considered more practicable, the use of chemical oxidative techniques for the removal of trace quantities of soluble lead from an effluent was investigated on a laboratory scale (Ref. 40). In this particular application the *insoluble* lead was already removable by other techniques to acceptable levels. However, in order to meet effluent regulations, more of the *soluble* lead had to be removed. Potassium permanganate, hydrogen peroxide, and sodium hypochlorite were tested and found to convert portions of the soluble lead as described below:

	Initial Soluble Lead Concentration	**Final Soluble Lead Concentration**
Potassium permanganate	14 ppm	4-7 ppm
Hydrogen peroxide	14	9
Sodium hypochlorite	14	9-10

The chemical oxidation processes did not appear economically practical for the application in question; reagent costs alone would have exceeded $1 million per year.

C. POTENTIAL APPLICATIONS TO WASTE TREATMENT

Chemical oxidation should be explored further for the treatment of any of the wastes discussed in the previous section for dilute waste streams. The use of chemical oxidation for more concentrated wastes should receive careful evaluation for their comparative economics, the additional pollutant load caused by the addition of chemicals to the waste stream, and the ability for the treatment to handle the concentrations in question from a safe processing standpoint.

The following statements can be made about suitable waste streams:

Physical Form of Waste – gases and aqueous solutions are acceptable. Chemical oxidation would have limited applicability to slurries and sludges unless it were possible to dilute them for treatment. Some waste streams could possibly be contacted for the necessary time with a sufficient excess of oxidant and sufficient mixing to effect detoxification. Tars also would find limited applicability.

Chemical Nature of Contaminants – Some heavy metals can be oxidized for easier removal in a subsequent treatment step. Unsaturated organics in general are susceptible to chemical oxidation. Cyanides, sulfides, and sulfites can be treated. Phenolics, pesticides, aldehydes, and aromatic hydrocarbons also appear to be oxidizable by the use of appropriate chemical oxidants.

Concentration Range – Most of the applications to date are in water systems, containing dilute concentrations or oxidizable substances, generally not more than a few thousand ppm.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Total energy consumption, not including the energy required to produce the chemicals, is low for chemical oxidation. The only requirements are for pumping the waste and the oxidant and for mixing of the two to provide contact.

B. ENVIRONMENTAL IMPACTS

One disadvantage of chemical oxidation for waste treatment is that it introduces new metal ions into the effluent. If the level of these new contaminants is high enough to exceed effluent regulations, additional treatment steps will be required. Often these are steps such as filtration or sedimentation. Potassium permanganate used to treat wastes will be reduced to MnO_2 in the process. This can be reduced by filtration to levels less than 0.05 mg/l in the final effluent.

On the other hand, oxidation with hydrogen peroxide adds no harmful species to the final effluent (except perhaps excess peroxide) since its product is water.

Whether the products of incomplete oxidation are an environmental hazard depends upon the specific situation. Cyanate, the product of potassium permanganate oxidation of cyanide, is not completely oxidized. Treatment with another oxidant, or acid hydrolysis after permanganate oxidation can oxidize the cyanide completely to CO_2 and N_2. Cyanate, however, is at least a thousand times less toxic than free cyanide. The conversion of benzidine to the products of diazotization is another case in which the treated waste is less hazardous than the first, but still is considered a problem.

Often the extent to which excess chlorine must be added for waste oxidation is such that the residual chlorine in the effluent becomes a problem. Careful in-process control or recycling of the oxidizing solution may be necessary to reduce this level to meet regulation limits. Also, hydrogen peroxide has been used as a reducing agent in some applications as an "anti-chlor" to destroy the chlorine remaining in the stream after purification.

With the exception of escape of chlorine, which is a potential hazard wherever chlorine is used, the only other air emission problem identified in this study was the possible production of HCN from the destruction of cyanide wastes when the reaction medium is allowed to become acidic.

From most chemical oxidations there will be a residue for disposal unless the concentration of the waste constituent is so low that the oxidant waste products (if any) and the oxidized (and de-toxified) waste can be carried away with the effluent. Most of the residue develops from the use of caustic or lime slurry with chlorine gas in alkaline chlorination. Smaller amounts of residue result from oxidations using hypochlorites. The only waste which appears particularly troublesome is the sludge which can develop in the oxidation treatment of cyanides when iron and certain other transition metal ions are present. In this form (ferrocyanide, for example), *the cyanide cannot be easily reached for further oxidation.*

C. ECONOMIC ANALYSIS

We have prepared a preliminary cost estimate for installation and operation of a facility for the chemical oxidation of cyanide waste from a plating operation using alkaline chlorination. The data presented in Table 3 are expressed in 1976 dollars. The stream characteristics and chemical requirements we have assumed are:

Stream Flow:	1000 gallons per day
Treatment:	batch
Influent Concentrations:	7000 ppm copper cyanide 1000 ppm sodium cyanide
Effluent Concentrations:	0 ppm cyanide
Raw Material Dosage:	NaOH 95 pounds /day Chlorine 227 pounds /day

The operating cost is estimated to be nearly $230 per 1000 gallons. This appears to be rather high for a cyanide waste stream; however, in this example, we have chosen a very highly concentrated waste in an attempt to approximate the kind of waste which is out of the realm of wastewater treatment. Because plating baths of this concentration are rarely disposed of, there is no data in the published literature for comparison. For a less highly concentrated cyanide waste (100 ppm copper cyanide and 100 ppm sodium cyanide) the capital investment would be approximately that of the system outlined in Table 3. The operating cost would be in the range of $170 per 1000 gallons.

TABLE 3

ESTIMATED OPERATING COSTS FOR OXIDATION

Basis: Batch Treatment of 1,000 GPD of Concentrated
Cyanide Wastes; 240 Days/Year Operation

Capital Investment: $100,000

Variable Costs	**Annual Quantity**	**Cost per Unit Quantity**	**Annual Cost ($)**
Operating Labor	2,000 MH	$12.00/MH	$ 24,000
Chemicals			
Sodium Hydroxide	11.5 tons	$290/ton	3,500
Chlorine	29.5 tons	$175/ton	4,800
Total Chemical Costs			
Utilities			
Electricity	12,000 kWh	$0.02/kWh	240
Cooling Water	360 M gal	$0.45/M gal	160
Total Utilities			400
Maintenance @ 4% of Investment			4,000
Total Variable Costs			$ 36,700
Fixed Costs			
Taxed Insurance @ 2% Investment			2,000
Capital Recovery (10 yrs @ 10%)			16,300
Total Fixed Costs			18,300
Total Annual Costs			$ 55,000
Unit Cost, $/10^3 Gallons			$229.20

Source: Arthur D. Little, Inc., estimates.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

A. BENEFITS AND LIMITATIONS OF THE PROCESS

Chemical oxidation can often detoxify certain hazardous wastes.

Chemical oxidation is suitable for streams with low-to-moderate concentrations of oxidizable material.

The technology is available and has documented use in industry and for waste treatment (primarily for wastewater treatment).

Chemicals are the major portion of the operating costs. As the waste becomes more concentrated this factor may become prohibitive.

Chemical oxidation is likely to be cost-effective for the less concentrated hazardous wastes. Other treatment methods are likely to be more cost-effective for other applications but not exclusively.

The equipment used in the process is simple to obtain and use. There is limited use of instrumentation and there are minimal heating and cooling requirements.

Energy requirements are not significant.

Addition of the oxidants into the waste stream may introduce additional pollutants into the final effluent requiring further treatment.

B. PROJECTED IMPROVEMENTS IN EQUIPMENT AND MATERIALS

There are few developments related to equipment and materials that are expected to expand the use of chemical oxidation past the current applications. As the problems of hazardous waste disposal become better defined, it is expected that new applications for chemical oxidation will be developed through additional research.

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B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD (partial listing)

1. Experts

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Cochrane Environment Systems, Crane Co., King of Prussia, Pennsylvania 19406

Orion Research, Inc., Cambridge, Massachusetts 02138

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Nelson Chemical Co., Detroit, Michigan 48233.

Frontier Chemical Co., Niagara Falls, New York 14302.

Boeing Corp., Wichita, Kansas 67202

LTV Corp., Grand Prairie, Texas 75050

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Bio-Ecology, Grand Prairie, Texas 75050.

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OZONATION

Prepared by

Judith C. Harris

I. CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

Technology for large-scale ozone application is well developed. Applications to industrial wastes are not numerous, but feasibility has been demonstrated for cyanides and for phenols. Laboratory and pilot studies have demonstrated potential for ozone treatment of other oxidizable hazardous species including chlorinated hydrocarbons, polynuclear aromatics, and pesticides.

Ozonation can be expensive but is likely to be economically competitive with other processes for treatment of dilute (< 100 ppm) waste streams. The dominant expense component (capital cost and power requirements) in ozonation systems is the cost of ozone generation. Any improvement that reduces ozone demand (e.g., irradiation by UV light) or improves efficiency of utilization (e.g., better ozone/waste mixing systems) may dramatically improve economic feasibility, when considered in the light of total system cost effectiveness. Labor requirements for operation and maintenance of ozone systems are low. Space requirements are also low.

B. RECOMMENDATIONS

We recommend that ozonation be considered for treatment of any aqueous or gaseous waste stream containing less than 1% of oxidizable hazardous component(s). It can be particularly useful as a final treatment process in applications where partial treatment is already installed, but where more complete removal of oxidizable substances is required to meet effluent discharge criteria. Ozonation should be considered as a preliminary treatment for more concentrated wastes that are oxidizable but are not amenable to other treatment techniques.

A more exhaustive study should be made of the literature references on susceptibility of various species to ozonation. Laboratory studies should be conducted using carefully controlled conditions to evaluate the effectiveness of ozone treatment of various pollutants of current concern. Additional support should be given to research and development programs aimed at more efficient ozone generation and at improved ozone/water mixing.

II. PROCESS DESCRIPTION

A. BACKGROUND

Ozonation consists of treatment with ozone, O_3, which is an extremely reactive gas. Ozone cannot be shipped or stored, and must be generated on site immediately prior to its application.

Ozone is a very powerful oxidizing agent. Organic chemists have long made use of the ability of ozone to cleave carbon-carbon bonds in synthetic and structure-determination procedures. There are abundant literature references to the mechanisms and products of ozonation of a variety of organic compounds. References to reactions of inorganic chemicals with ozone are fewer, but not scarce. These literature data can be used to make preliminary choices of industrial waste streams suitable for ozonation.

In addition to high chemical reactivity, ozone has powerful antibacterial and antiviral properties. The disinfecting as well as oxidizing power of ozone has been responsible for virtually all of the large-scale applications of ozone to date. Ozone is widely used in Europe for quality improvement and disinfection of potable water. Technology for application of ozone, at doses of a few ppm, to millions of gallons per day of aqueous streams, is therefore highly developed. This technology can be readily adapted to treatment of selected industrial waste streams.

B. UNDERLYING PRINCIPLES

Ozone is a powerful oxidizing agent, as illustrated by the following redox potentials:

$$O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O \qquad E_o = 2.07v$$

$$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O \qquad E_o = 1.70v$$

$$\tfrac{1}{2}Cl_2 + e^- \longrightarrow Cl^- \qquad E_o = 1.36v$$

It is sufficiently strong to break many carbon-carbon bonds and even to cleave aromatic ring systems (e.g., conversion of phenol to 3 molecules of oxalic acid). Complete oxidation of an organic species to CO_2, H_2O, etc., is not improbable if ozone dosage is sufficiently high.

1. Reactivity of Substance

One variable over which there is very little control is the intrinsic rate of chemical reaction of ozone with the oxidizable substance. Two sets of literature data on the results of batch ozonation experiments will serve to illustrate the wide range of reactivity. The values of "Refractory Index" (RFI) in Table 1 are calculated indices of resistance to ozone oxidation for dilute (50-100 mg/l) aqueous solutions of the compounds listed. The RFI values, though defined in units of hours, are numerically equivalent to the number of pounds of ozone per pound of compound that would be required to achieve 50% conversion of compound in one hour. Clearly, acetic acid and ethanol are much more resistant to ozone than is phenol.

TABLE 1

RESISTANCE OF SELECTED SPECIES TO OZONE OXIDATION

Compound	**RFI (hours)***
KCN	0.41
Color (-units)	0.66
Complexed Cd-cyanide	0.96
Phenol	4.4
Ammonium Ion	8
Glycine	19.7
Ammonium Palmitate	27.3
Glycerol	112
Ethanol	245
Complexed Ferricyanide	270
Acetic Acid	>1,000

*"Refractory Index" defined as follows:

$$RFI = \frac{B_c^\circ \text{ (mg/l) } t_{1/2} \text{ (hrs)}}{A^\circ \text{ (mg/l)}}$$

B_c° = cumulative ozone dose applied up to $t_{1/2}$.

$t_{1/2}$ = time for 50% [conversion of] oxidizable material (measured by decrease in TOC (Total Organic Carbon) for organic species and by specific analysis for inorganic compounds).

A° = initial concentration of compound listed.

Source: Ref. 1.

Table 2 contains data from another study (Ref. 2) of the percentage COD reduction accomplished for given hours of ozone treatment time. These data are for aqueous solutions with initial concentrations of ≥1 g/l of oxidizable substrate. Again, the results reveal a wide range of susceptibility to ozone oxidation. Furthermore, it is apparent that in several cases (e.g., diethylene glycol, ethylene glycol, formalin, methanol) there is an initial rapid decrease in COD, followed by a period in which no further reduction occurs as ozonation continues.

TABLE 2

REDUCTION IN COD AS A FUNCTION OF OZONE TREATMENT TIME

Compound	Concentration (g/l)	Volume Treated (liters)	O_3 (g/hr)	% COD Reduction for Given Hours of Treatment Time 2	4	6	8	12	16	24
Acetic Acid	1	3	2.45	0	0	0	0	0	0	0
Benzyl Alcohol	1	1	0.5	10	26	–	58	–	–	–
Diethylene Glycol	1	3	1.47	18	27	27	30	30	30	30
Ethylene Diamine	1	1	0.5	7	26	–	33	–	–	–
Ethylene Glycol	1	1	0.5	9	17	–	31	–	–	35
Formalin	5.0	3	2.28	10	20	29	36	44	48	53
Glycine	1.0	3	1.0	0	0	0	0	0	0	0
Hydroquinone	1	1	0.5	25	46	–	–	–	–	–
Hydroxylamine Sulfate	1	3	1.88	41	58	67	72	77	78	–
Maleic Acid	(not given)	3	2.44	62	73	79	83	89	92	95
Methanol	1	3	2.12	8	13	17	21	27	31	37
Potassium Ferricyanide	11.0	2	4.0	1	2	3	4	6	7	11
Sodium Formate	2.0	3	1.4	42	63	75	83	93	98	–
Sodium Thiocyanate	1	1	0.5	88	90	90	–	–	–	–
Sodium Thiosulfate	1	1	0.5	94	97	–	–	–	–	–

Source: Ref. 2.

This observation does not imply that, in the case of ethylene glycol, for example, 65% of the material originally present is unchanged after extended ozonation periods. What it does imply is conversion of the original oxidizable compound, ethylene glycol, to an intermediate, in this case glycolic acid, which is resistant to further oxidation by ozone. However, the glycolic acid is oxidizable under the conditions of a COD determination, so complete conversion of ethylene glycol to glycolic acid leaves a residual COD of about 60% of the original value.

$$HOCH_2CH_2OH \xrightarrow{O_3} HOCH_2COOH + O_2$$

ethylene glycol	glycolic acid
COD 2.5 moles O_2/mole	1.5 moles O_2/moles

Rosen (Ref. 6) has compiled a list of a number of environmentally undesirable compounds which have been reported as destroyed by ozonation. In many cases the original reports were qualitative (e.g., organoleptic analysis) or semi-quantitative experiments, and experimental details were incomplete. The compounds are listed in Table 3.

TABLE 3

COMPOUNDS REPORTED TO BE SUSCEPTIBLE TO OZONATION

Detergents

Alkyl benzene sulfonate
Anionic Detergent
Non-ionic Detergent

Phenols

Phenol
o-, m-, and p-cresols
Cathechol
Xylenols

Chlorinated Hydrocarbons

Chlorobenzenes

Pesticides

DDT
α-BHC
Dieldrin
Malathion
Methyl parathion
Aldrin

Aromatic Hydrocarbons

3, 4-Benzpyrene
Pyrene
1, 2-Benzanthracene
3, 4-Benzfluoranthene
11, 12-Benzfluoranthene
Biphenyl

Source: Ref. 6.

2. Products of Ozonation

It was noted above that complete oxidation to CO_2 could be achieved in some ozonations. This has been demonstrated in laboratory experiments in which virtually complete reduction of COD was achieved. In other cases, oxidation is not complete, either because of insufficient ozone dosage or because of formation of oxidized intermediates that resist further ozonation.

Whether or not partial oxidation constitutes satisfactory treatment depends on the criteria which have been established for a particular waste stream and/or ultimate disposal site. If, for example, the objective of a treatment process were deodorizing a foul gas stream containing amines, then ozone oxidation to the corresponding relatively non-odorous, amine oxides would probably meet the criteria for discharge to the atmosphere. However, if the amines were contained in an aqueous stream and the effluent guidelines were expressed in terms of COD, the same conversion of amine to amine oxide would not accomplish a significant reduction in the critical parameter (COD). In yet other cases, the criterion for treatment may be destruction or detoxification of a specific stream component. In these cases complete conversion of the original component to an oxidized intermediate would meet the treatment objective.

Table 4 lists the products typically expected from ozonation of a variety of oxidizable materials. In some cases, the species listed is a primary ozonation product which can be further degraded by extended ozone treatment.

3. Ozone Dosage

In reports of ozonation reactions on processes, ozone dosage is commonly expressed in two ways: ppm of ozone and pounds of ozone per pound of stream contaminant treated.

The ozone dosage in ppm ozone is obtained by multiplying the flow rate of ozonized gas by the concentration of ozone in the gas and dividing by the flow rate of the waste stream. In disinfection applications, ozone doses of <4 ppm are typical for secondary treated streams. In industrial waste treatment applications, it is more usual to supply ozone at 10, 20, or 40 ppm.

The second measure of ozone dosage, the weight ratio of ozone to contaminant treated, is obtained from the ppm ozone applied, the residence time of the waste stream in the ozone contact chamber, and the concentrations of contaminant in the influent and effluent streams. The ratio can vary from less than one (0.33 parts ozone per part of cyanide under optimum conditions) to very large values (ca 80 parts ozone per part of phenol for very low concentrations of phenol). In most applications the amount of ozone applied is 1.5 to 3 pounds of ozone per pound of contaminant removed.

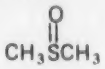
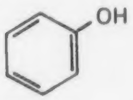
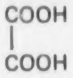
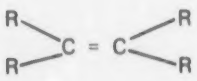
The two measures of ozone dosage are clearly not entirely independent. However, it should be noted that four hours' treatment at 10 ppm ozone will not, *a priori*, produce the same result as one hour of treatment at 40 ppm ozone. The optimum combination of instantaneous ozone dose (ppm) and contact time must be determined for each case.

The extent of oxidation obtained will increase as either the weight ratio or the instantaneous dose is increased, up to certain limits defined by the fundamental chemistry of the ozonation reaction(s). However, there are practical and economic constraints on the amount of ozone which can actually be applied. Ozone is generally produced at a concentration of about 1% by weight in air (2% maximum) or 2-3% by weight in oxygen (6% maximum). This corresponds to 650 cu ft of air, or 325 cu ft of oxygen, per pound of ozone delivered. To produce an instantaneous dose of 40 ppm O_3 in a waste stream, one would have to supply 208 cu ft of ozonized air per 1000 gallons (133 cu ft) of waste. This would require very efficient mixing indeed to achieve effective mass transfer. With a Venturi mixer, for example, the maximum ozone dose obtainable from ozonized air is 15 ppm. These calculations indicate why there is intense interest in design and development of more efficient ozone delivery systems.

At a fixed instantaneous dose (ppm), the extent to which the total ozone dose (pounds O_3/pound of contaminant) can be varied is limited primarily by economic constraints. The controlling variable is the stream volume, which determines the size of ozone contact

TABLE 4

PRODUCTS OF OZONATION OF VARIOUS COMPOUNDS

Species	Ozonation Product	Comments
Chromium (III) Cr^{+3}	Chromium (VI) CrO_3	
Cyanide CN^- (free)	Cyanate CNO^-	Cyanate can be further degraded to CO_2
Ferrocyanide $Fe(CN)_6^{-4}$	Ferricyanide $Fe(CN)_6^{-3}$	Used in regeneration of photo bleach
Ammonia NH_3	Nitrate NO_3^-	Fairly slow
Sulfide CH_3SCH_3	Sulfoxide  $CH_3\overset{\overset{O}{\|}}{S}CH_3$	Reduces or eliminates odor problems
Amine $(CH_3CH_2CH_2CH_2)_3N$	Amine oxide $(CH_3CH_2CH_2CH_2)_3NO$	
Alcohol CH_3OH	Aldehyde CH_2O	Evidence for stepwise oxidation is clear
Aldehyde CH_2O	Carboxylic acid $HCOOH$	
Carboxylic acid CH_3COOH	no reaction	
Phenol 	Oxalic acid  $\begin{array}{c}COOH\\ \vert\\ COOH\end{array}$	By way of quinone and intermediate, unsaturated acids
Alkene 	Aldehydes, ketones, carboxylic acids $R_2C = O$ RCOOH $RHC = O$	

chamber required for a given retention time. For hazardous waste treatment, the longer retention times usually require 10 minutes to one hour application of ozone in several stages.

4. pH Dependence

Ozone is more soluble and more stable in acidic than in basic solutions. However, the rate of most ozonation reactions is relatively insensitive to pH, and it is rarely worthwhile to adjust pH prior to ozonation. The cost of the neutralization process will frequently offset any gains in ozonation efficiency.

One exception to this generalization is cyanide ozonation. The cyanate formed initially hydrolyzes more rapidly in alkaline media. If complete conversion of cyanide to CO_2 is required, acidic streams should be adjusted to a pH of about 9 before ozonation. (Ammonia ozonation is also more effective in alkaline solution, but ozonation is unlikely to be the treatment method of choice for this species.)

5. Catalysis – Photolysis

Aside from the observation that small amounts of Cu(II) catalyze the ozonation of cyanide, there have not been many studies of chemically catalyzed ozonation.

The catalytic effect of UV light on ozonation reactions has been extensively studied at Houston Research. Their laboratory and pilot scale research have convincingly demonstrated that a combined UV/ozone system can extend the utility of ozonation dramatically. Some compounds that are highly resistant to ozone alone can be ozonated in the presence of UV light. The RFI values in Table 1 should be compared with the following values obtained in the combined UV/O_3 system: Glycine, 6.0; ammonium palmitate, 7.2; glycerol, 7.4; ferricyanide, 8.6; ethanol, 41; acetic acid, 47. The ozonation of acetic acid to CO_2 and water is more than 25 times faster in the presence of UV light. One large-scale (mgd) plant using the Houston Research "oxyphotolysis" process is in operation, and another is scheduled for July start-up.

With the exception of the ferricyanide species, which is known to be photosensitive, the compounds studied have weak UV absorptions. Ozone itself, however, does absorb UV light, and it seems that the mode of action of the UV/O_3 process is "activation" of ozone itself. Whatever the detailed mechanism may be, the possibilities of further exploitation of this system are exciting. For species that are inherently susceptible to ozone, the addition of UV light can reduce ozone demand by a factor of two. One can thus achieve the same degree of treatment for much less cost or much more treatment for about the same cost.

Although the UV/O_3 system seems too complicated at first inspection, it must be remembered that ozone generation is by far the most expensive part (capital and operation) of an ozonation system. One can purchase and operate many UV lamps with the money saved by reducing ozone demand from, say, 500 pounds per day to 250 pounds per day.

C. OPERATING CHARACTERISTICS

1. Stream Characteristics

Ozonation is practical only for treatment of streams with low concentrations of oxidizable material. If one uses the rule of thumb of two pounds of ozone required per pound of oxidizable material, then a large commercially available ozone generator, which produces 500 lbs/day of ozone, could treat:

1 mgd at 30 ppm of oxidizable matter

.3 mgd at 100 ppm of oxidizable matter

30,000 gd at 1000 ppm (.1%) of oxidizable matter.

It is quite possible to install more than one of these large ozone generators (at increased capital cost), but it is almost certainly not realistic to consider ozonation of 30 mgd of a stream with 2% phenol!

Because ozone is a relatively non-selective oxidizing agent, the stream to be treated cannot contain appreciable oxidizable material other than the waste component. This rules out some non-aqueous solvents, which are easily oxidizable organics. Sludges, slurries, and tars are also unlikely candidates for ozonation, unless they could be greatly diluted and dispersed in water. Even if these wastes were primarily composed of non-oxidizable material, the problems of mixing ozonized air with the semi-solid waste would be formidable. It might be possible to ozonate suitable bulk solids or powders in a fluidized bed reactor, but we know of no attempts to do so. Of course, the waste would still be subject to the restriction of low levels of oxidizable material. (It should be noted that the ozonized air produced by modern generators is at low pressure (ca 8 psi) and would not suffice to fluidize the waste.)

In conclusion, ozonation is best suited for streams that are aqueous or gaseous, and contain low levels of oxidizable material. There are no inherent restrictions on levels of dissolved or suspended solids in an aqueous stream, so long as these do not contain oxidizable material that can compete for ozone under the conditions of treatment required to remove the polluting component.

2. How Process Operates

In an ozonation process, ozone is generated at a concentration of ≤2% and a pressure of <15 psi, from a stream of air (or oxygen) previously dried to a dew point of -50°C or lower. The ozonized air is then introduced into a contact chamber designed to ensure good mixing with the waste stream.

For aqueous wastes, various devices have been used to form an emulsion of ozonized air (or oxygen) with water. Most of the ozone installations in Europe, which are intended for disinfection and/or final "polishing" of water, have used either a porous diffuser or a Venturi type injector. The Venturi injector is relatively simple and inexpensive, but the efficiency of ozone absorption is poor. The porous diffuser is relatively efficient and can be used to supply fairly high ozone dosages. Another alternative is an impeller which aspirates the ozonized air and water and mixes them by means of a high velocity rotor. Other types of emulsification systems, including static and sonic mixers, have been investigated but are not in widespread use.

The contact chamber is designed so that the liquid depth is at least 15 feet; this minimizes the possibility of escape of unreacted ozone. Residence time of the liquid is 10 minutes or more. Most modern installations utilize a counter-current flow of waste stream and ozonized gas, but co-current designs are not uncommon. The rationale for counter-current flow patterns is that maximum ozonizing power is applied to the most dilute waste, where removal of trace quantities is most difficult. Co-current design most closely approximates a plug flow reactor that maximizes ozone mass transfer. Two or more staged reactors are frequently employed.

A porous diffuser is used for application of ozone to gaseous waste streams if the ozonized air is generated at a positive pressure. Mixing is accomplished by diffusion, sometimes aided by the installation of baffles to create turbulent flow. In systems which generate ozonized air at atmospheric pressure, a wet scrubbing process is used; a fine mist of ozone-saturated water is sprayed into a contact chamber. Contact times for ozonation of gaseous waste streams are typically 5-60 seconds.

Both for economic and safety reasons, the concentrations of ozone leaving the contact chamber are carefully monitored. All modern installations are equipped with on-line, real-time instrumental ozone monitors, which dictate a reduction in ozone generator power, and hence ozone output, when effluent ozone levels exceed a preset level. This cut-back level is typically 0.05 ppm; this is higher than the ozone threshold odor level of .01 to .02 ppm but below the OSHA Threshold Limit Value of 0.1 ppm. (The dosage of ozone required to produce symptoms of irritation in man is well above 0.1 ppm for moderate exposure times [ca 100 min].) In some applications, the "spent" ozonized air from the principal contact chamber is cycled back to provide pretreatment of the incoming aqueous waste.

The aqueous or gaseous waste stream effluent should also be monitored regularly to ensure adequate destruction of the hazardous component(s). Where an appropriate on-line measuring system is available, this signal can also be incorporated into a feedback system to the ozone generator. The supply power, and therefore the applied ozone dosage, can be automatically increased to achieve more complete treatment.

The waste stream effluent from ozonation of a gaseous waste is discharged directly to the atmosphere. An ozonated aqueous waste stream may be discharged to a sewer or to a natural body of water. In the latter case, ozonation provides benefit over and above the detoxification of hazardous waste components: water leaving an ozone contact chamber is generally saturated or supersaturated with respect to oxygen.

3. Output Streams

The output stream from an ozonation process is physically similar to the input stream, although color and turbidity are often reduced. Some insoluble species, such as metal oxides, may be formed and must be separated by use of a post-ozonation settling tank. The chemical composition of the stream will be altered in favor of more oxygenated species. The COD of the effluent will be lowered, but the BOD may actually be higher. This latter effect is due to the conversion of biologically recalcitrant organics to biodegradable species.

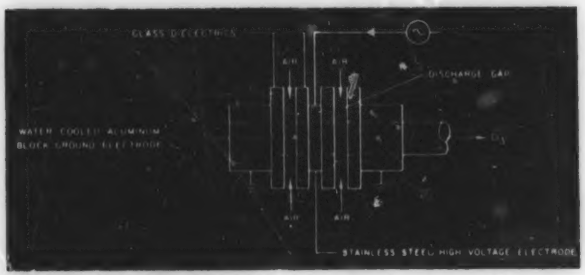
D. EQUIPMENT AND MATERIALS

In addition to the usual array of pumps, gauges and tanks, an ozonation system must include fairly specialized equipment for ozone generation, delivery and monitoring.

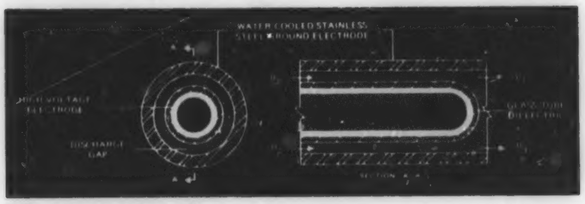
1. Ozone Generation

Ozone is produced by the facile reaction of oxygen molecules with oxygen atoms which are produced from O_2 by the action of ultraviolet light or an electric discharge. The photochemical production of ozone is important in stratospheric chemistry, but commercial ozone generators are all of the electric discharge type.

In an electric discharge ozone generator (Figure 1), an oxygen-containing gas is passed between two electrodes, coated with a dielectric material such as borosilicate glass. A high voltage (5-20 kilovolts) ac (50-10,000 Hz) potential is maintained across the electrodes. Generator output is varied according to signals from control instrumentation, by modulating voltage or frequency. The dielectric material provides a uniform glow discharge across the electrode gap, preventing an arc discharge. The geometry of the electrode system is variable; electrodes may be tubular or flat and may be mounted either horizontally or vertically. Tubular generators are used for most high capacity systems, although one manufacturer uses a Lowther Plate type for all sizes of generator. Materials that come in contact with ozone must be corrosion-resistant; stainless steel, unplasticized PVC, aluminum, Teflon and chromium-plated brass or bronze are all suitable.


GLASS DIELECTRICS
AIR
AIR
DISCHARGE GAP
WATER COOLED ALUMINUM
BLOCK GROUND ELECTRODE
O_3
AIR
AIR
STAINLESS STEEL HIGH VOLTAGE ELECTRODE

Otto plate type generator unit


WATER COOLED STAINLESS
STEEL GROUND ELECTRODE
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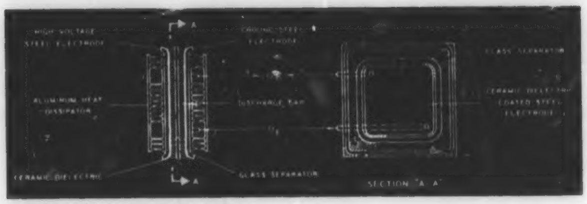
HIGH VOLTAGE
ELECTRODE
DISCHARGE
GAP
A
GLASS TUBE
DIELECTRIC
SECTION A-A

Tube type generator unit


A
HIGH VOLTAGE
STEEL ELECTRODE
GROUND STEEL
ELECTRODE
GLASS SEPARATOR
ALUMINUM HEAT
DISSIPATOR
DISCHARGE GAP
CERAMIC DIELECTRIC
COATED STEEL
ELECTRODE
O_3
CERAMIC DIELECTRIC
A
GLASS SEPARATOR
SECTION "A-A"

Lowther plate generator unit

FIGURE 1

Ozone production is inherently inefficient, as about 10% of the ac energy supplied is used in formation of ozone. In order to maximize efficiency, the oxygen-containing gas must be free of dust and organic matter and must be dry (dew point -50°C), since water accelerates the decomposition of ozone. Ozone is also thermally unstable, so provision must be made for air or water cooling of the high voltage electrodes. This requires about 1/3 gpm of cooling water at 21°C per lb O_3/day.

Most efficient ozone production is obtained when oxygen is used as the feed gas to the ozonizer, and such feed may be required for some hazardous waste treatment. With air as feed gas, output of ozone is about two times lower in quantity and concentration; maximum yields from air are about 25 g/m^3 or 2% by weight. Choice of oxygen, air or some intermediate oxygen concentration for the feed gas will depend on economic factors. Oxygen is a viable choice only for fairly large scale systems (>0.5 mgd) or those where inexpensive oxygen is already available (steel mills, for example, and some biological treatment plants). The availability of pressure-swing oxygen enrichment systems may make oxygen feed more practical in the future.

Outputs and power requirements of typical modern commercial ozone generators are shown in Table 5. These data are for air feed of the ozonizer. Yields can be increased by use of oxygen, with reduction of power requirements (kWh/lb) by about a factor of two. It should be emphasized that all of these generators produce ozone at a concentration of a few percent by weight in air or oxygen; and that the ozonizer effluent is pressurized to no more than 15 psi.

TABLE 5

OZONE OUTPUT AND ENERGY REQUIREMENTS OF OZONE GENERATORS
(Air Feed)

Generator Type	Ozone Output* Single Element (lb/day)	Ozone Output* Typical Unit (lb/day)	Specific Power* (kWh/lb of O_3)
Vertical Plate Otto	1.4 (3.6)	115 (300)	8.7 (7.2)
Horizontal Plate**	1.0	125	9.0 (2000 Hz)
Horizontal Tubular	0.8	390	7.7
Verticular Tubular	1.0 (3.1)	>300	7.7 (7.4)

*Values in parentheses are for operation at 500-600 Hz. Others are for 50-60 Hz.
**Personal communication from H.M. Rosen.

Source: Ref. 5.

Suppliers of ozone-generating equipment are listed below. (This list may not be all-inclusive.)

Crane Cochrane Environmental Systems
King of Prussia, Pennsylvania 19406

PCI Ozone Corporation
Stamford, Connecticut 06902

TII Ecology, Inc.
Lindenhurst, New York

Union Carbide Corporation
Tonawanda, New York

Welsbach Ozone Systems
Philadelphia, Pennsylvania

2. Contact Systems

The two ozone/water mixing systems in most widespread use are Venturi mixers and porous diffusers. With the Venturi mixer, ozonized gas and waste flow co-currently, and ozonized gas flow is limited to 30-60% of the liquid volume flow. In a porous diffuser system, a counter-current flow is usual, and gas flow may be up to twenty times the liquid flow.

In some systems the contact column is a packed bed. This increases surface area and increases the rate of mass transfer of ozone into solution. One equipment manufacturer, TII Ecology, has been using ultrasonics in conjunction with ozonation; this also increases surface area. Depending on the extent of treatment required, it may be necessary to incorporate two or more contact stages. These may be of different types. Where oxygen is used as a feed gas to the ozonizer, it is usual to recycle the effluent from the contact chamber.

3. Control Instrumentation

Modern ozone systems are completely automated. An ozone monitor provides continuous on-line monitoring of the ozone concentration in the gaseous effluent from the contactor. If the concentration of ozone exceeds a preset level, usually 0.05 ppm, the voltage or frequency of the ozone generator is reduced.

Depending on the characteristics of the waste, the system may also include on-line monitoring for hazardous species concentration in the liquid effluent. When appropriate instruments exist, the output signals may feed back to the ozonator to increase ozone dosage as necessary.

The system also includes automatic shutoff provisions in the event of loss of ozonator coolant.

Finally, an ambient air ozone monitor is used which sounds an alarm and shuts off power to the ozonator in the event of gross leaks of ozonized air.

4. Flow Diagrams

Figure 2 shows process flow diagrams for typical ozonation systems.

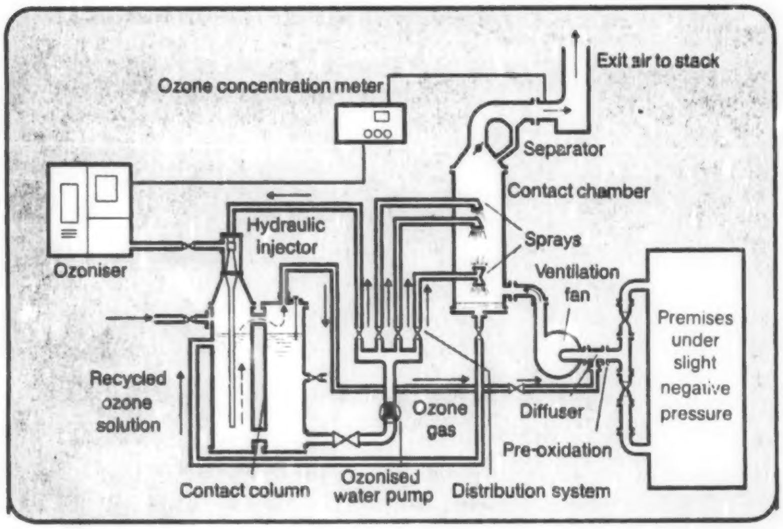
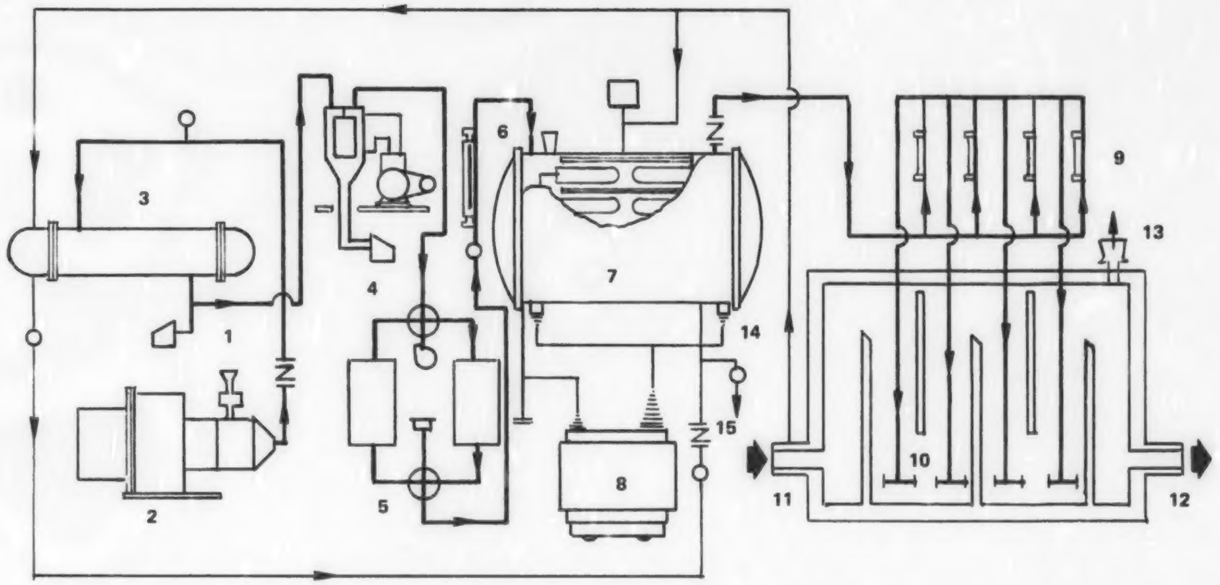

Exit air to stack
Ozone concentration meter
Separator
Contact chamber
Hydraulic injector
Sprays
Ozoniser
Ventilation fan
Premises under slight negative pressure
Recycled ozone solution
Ozone gas
Diffuser
Pre-oxidation
Contact column
Ozonised water pump
Distribution system

FIGURE 2a VAR PROCESS COMBINES OXIDATION BY ZONE WITH PHYSICAL SCRUBBING



1 Air Inlet
2 Rotary Air Compressor
3 Air Cooler
4 Refrigerator
5 Air Drier
6 Air Flow Measurement

7 Ozoniser
8 H.T. Transformer
9 Ozonised-Air Measurement
1C Porous Diffusers
11 Inlet Ozonised-Air-Water Emulsification Tank

12 Outlet Ozonised-Air-Water Emulsification
13 Air Return to Atmosphere
14 Cooling Water Supply
15 Cooling Water Discharge

FIGURE 2b OZONATION PLANT SCHEMATIC ARRANGEMENT

III. APPLICATIONS TO DATE

A. PRINCIPAL CURRENT APPLICATIONS

Ozone treatment has been used in Europe and elsewhere in large-scale installations for years, for disinfection of water supplies. Over 500 such installations are in use worldwide. Within the past few years, there have been a number of pilot and full-scale applications of ozone to treatment of municipal sewage plant effluents in the United States. A partial listing of these installations is:

Blue Plains, Washington, D.C. (pilot)
Indiantown, Florida (full-scale)
Woodlands, Texas (full-scale)
Springfield, Missouri (full-scale)

These applications have little relevance to this contract, except to illustrate that ozone technology is well developed, and to provide a basis for estimation of operating parameters.

The following are some selected examples of application of ozone to hazardous waste management problems.

1. Gaseous Effluents

a. Wet oxidation ozonation is used to treat 50,000 m^3/hr of odorous gaseous effluent from a Swiss sewage works. Ozone dosage is 10-40 mg ozone/m^3 of treated air. Contact time is 5 sec.

b. Sulfide and other odors are removed from a rendering plant effluent (25,000 cfm) at an ozone dosage of 42 lb/day. Contact time is 5 sec.

c. Fermentation odors are removed from a pharmaceutical plant effluent (80,000 cfm) with an ozone contact time of 10 sec.

2. Liquid Effluents: Cyanide

a. At an installation in Kansas, 350 lbs/day of ozone are used to treat effluent containing cyanides, sulfides, sulfites, and other hazardous components. This ozonation follows biological waste treatment.

b. At the Michelin tire factories in Clermont-Ferrand, France, 3.5 lbs ozone/lb of cyanide are used to reduce cyanide levels in effluent from 25 mg/l to 0 mg/l. A flow of 90 gpm is being treated.

c. At a large chemical plant in France, UV/ozonation (Houston Research) is being used to treat several hundred gallons/min of waste containing 6 mg/l of $Fe(CN)_6^{-3}$. The effluent stream meets the standard of < 0.1 mg/l total cyanide.

In the process, oxidation of organics also occurs; the influent stream has TOC of 800 ppm and the effluent has a BOD of 30 ppm.

d. In the northeastern U.S. a small (< 10,000 gpd) electroplating facility uses ozonation as the primary treatment process in reducing CN^- levels (60 ppm) in plating wastes to below detectable levels.

3. Liquid Effluents: Dyestuffs

a. In Japan, a combination of ozonation and activated carbon adsorption has been used to remove color, BOD and COD from 3300 m^3/day of waste dyeing water.

4. Liquid Effluents: Phenols

a. An ozonation process for oxidation of phenols in coke oven wastes is in the start-up phase at Allen Wood Steel in Conshohocken, PA. An ozone dosage of 10 ppm reduces phenol from 10 ppb to <0.5 ppb.

b. An ozonation process for oxidation of phenols in wood products waste is in the start-up phase at Blandon F.P., Grand Rapids, MI. An ozone dosage of 10 ppm reduces phenol from 300 ppb to < 10 ppb.

c. At the Cities Service Refinery in Bronte, Ontario, Canada, ozonation is used for final removal of phenols from biologically treated effluents. The ozone is applied at 20-40 ppm and reduces phenol from 380 ppb to 12 ppb.

B. POTENTIAL APPLICATIONS TO WASTE TREATMENT

Ozonation should be further explored for two types of industrial waste treatment application: 1) as pre-treatment to make waste more amenable to treatment by another process, and 2) as sole or final treatment for dilute waste streams.

1. Preliminary Treatment By Ozonation

In application of ozone for preliminary treatment, no attempt is made to achieve complete oxidation of organics to CO_2, etc. Rather, the objective is to convert recalcitrant or refractory species to ones more readily handled by other methods.

a. Treatment of oil-water emulsions with small doses of ozone in some cases caused breakage of the emulsion.

b. Pilot studies at the 50 mgd Westerly Treatment plant in Cleveland, Ohio have indicated that ozonation of influent to a carbon adsorption system at a dosage of 5 ppm had a number of advantages:

- The COD reduction achieved in the carbon adsorption column was increased from 40% to 80%.

- The effective lifetime of the carbon was increased by at least a factor of three.

- The ozonated stream could be treated using a less expensive grade of carbon.

- The adsorption column remained aerobic, preventing leaching of iron and sulfur from the charcoal.

c. It has been observed in a number of studies that ozonation converts COD to BOD. It is probable that some waste streams, such as those containing aromatic or chlorinated hydrocarbons, or other species unsuitable for biological treatment, could be safely treated in biological municipal waste treatment plants after low dosage ozonation.

2. Sole Or Final Treatment By Ozonation

We recommend that ozonation be considered as a treatment process for any stream which contains <1% of oxidizable hazardous material. Examples of such streams are: contaminated gas streams from production or utilization of volatile hazardous materials (e.g., vinyl chloride monomer); contaminated aqueous streams from industrial washing or rinsing operations; plating wastes; effluents from other treatment processes (e.g., solvent extraction).

It should be stressed that the feasibility of ozonation as a treatment for a particular waste can be demonstrated conclusively only by laboratory and/or pilot tests on the waste (or a carefully simulated sample if the waste is to be the effluent from a treatment not yet installed). Such studies should include not only measures of the percentage decrease in original component or COD, but analysis of ozonation products.

The preceding caveat notwithstanding, the following statements can be made about suitable streams:

a. **Physical Form of Waste**

Gases and aqueous solutions are suitable. Slurries, sludges, tars, and solutions in oxidizable liquids are less suitable.

b. **Chemical Nature of Contaminants**

Fully oxidized species are obviously not suited to ozonation. However, ozonation can remove heavy metals ions by precipitating them as the oxides.

Inorganic cyanides, thiocyanates, carbonyls, sulfides, and sulfites can be converted.

Among organics, low-molecular-weight saturated acids (e.g., acetic), saturated hydrocarbons, pyridine, and chloroform appear to be *resistant* to ozonation.

Classes of compounds that are *susceptible* to ozonation include:

alcohols
aromatic hydrocarbons (including polynuclears)
carbonyl compounds
chlorinated aromatics (pesticides)
nitroso compounds
P and S compounds
phenolics
unsaturated hydrocarbons

Ozonation has also been reported as effective in reduction of "color" in paper mill effluents.

c. **Concentration Range**

It should be clear that the concentration of oxidizable waste that can be economically treated by ozonation will depend in part on the stream volume.

The statement that ozonation is practical only for streams with concentrations of oxidizable material less than 1000 ppm is based on a rough cost estimate of 1¢ per 1000 gal per ppm ozone applied. This can be combined with the "ballpark" estimate of 2 parts ozone (by weight) per pound of oxidizable contaminant to put an upper limit on the range that can be practically and economically treated.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Ozonation, using a corona discharge as the ozone source, is an energy intensive process. The best available estimates are that the process requires about 7 kWh/lb of ozone from air produced for the generator, plus an additional 3 kWh/lb O_3 for air drying. Total energy consumption is $\leqslant$ 12 kWh/lb O_3 applied to the waste. For oxygen recycle systems this becomes $\leqslant$ 6 kWh/lb O_3.

B. ENVIRONMENTAL IMPACTS

One of the advantages of ozonation is that the process leaves no inherent harmful residue. In aqueous "ozone demand free" solution, ozone decomposes to oxygen with a half-life of 20 to 30 minutes. For aqueous streams, the residual oxygen produced by ozone decomposition may be considered a beneficial residue. Ozone lifetime in a gaseous stream is somewhat longer, but in practice, stack effluents from gas ozonation processes are easily controlled to <0.04 ppm of ozone.

Whether products of incomplete oxidation constitute an environmental hazard must be assessed for each waste stream. In a number of cases it has been found that these products are less toxic and more biodegradable than the original waste components.

One of the advantages of ozonation systems over competitive processes is that they are relatively compact. This is partly due to the fairly short detention time required in the ozone contact chamber. This feature can be particularly attractive when a treatment process is to be installed in a pre-existing facility.

Ozone is recognized to be a toxic substance. Figure 3 shows the concentration ranges and exposure times which produce varying levels of toxic effects. The OSHA Threshold Limit Value (which represents an airborne concentration to which it is believed that nearly all workers can be exposed day after day without adverse effect) is 0.1 ppm of ozone. The odor of ozone is distinctive and serves as an effective warning signal at levels well below the toxic level; the threshold odor level is 0.01-0.02 ppm. Furthermore, all ozonation systems are equipped with monitors to detect ozone in gaseous effluents, which reduce power to the ozone generator if effluent levels exceed 0.05 ppm of ozone. Since ozone is generated at the same rate as it is applied to the waste and at low pressure (< 15 psi), the risk of exposure to high ozone levels is extremely small.

C. ECONOMIC ANALYSIS

We have prepared a preliminary cost estimate for installation and and operation of an ozonation facility for final removal of phenol from a biologically treated oil refinery effluent. The data presented in Table 6 are expressed in 1976 dollars. We have included in our estimate the cost of special materials of construction (e.g., stainless steel) for portions of the system in contact with ozone.

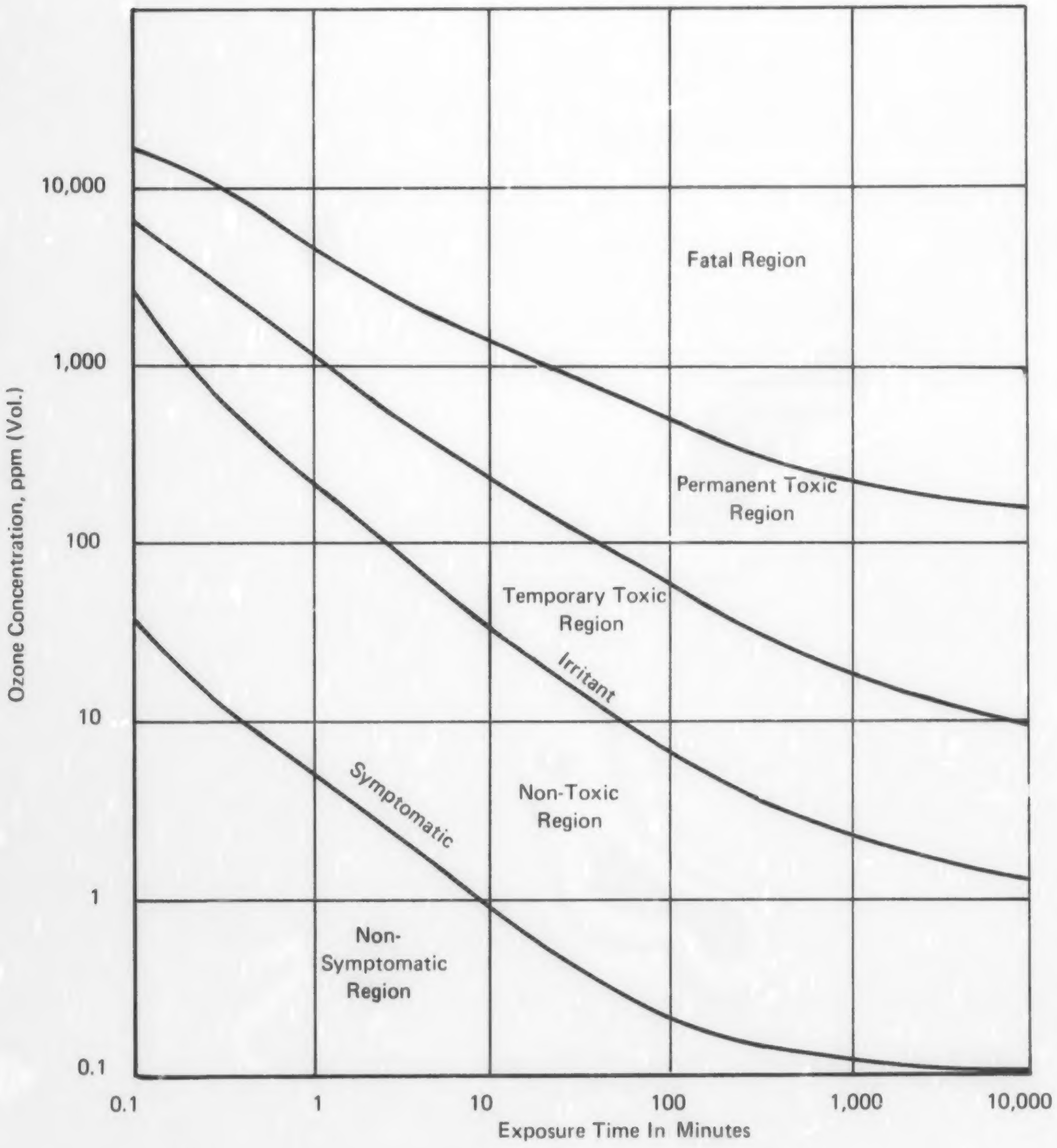


FIGURE 3 HUMAN TOLERANCE FOR OZONE

TABLE 6

PRELIMINARY COST ESTIMATE FOR REMOVAL OF PHENOL BY OXIDATION

Basis: 800,000 gal/day @ 0.38 ppm phenol
Estimated Capital Investment: $330,000

Variable Costs	**Annual Quantity**	**Cost per Unit Quantity**	**Annual Cost ($/yr)**
Operating Labor (including supervision and overhead)	3,000 hr	$12.00/hr	$ 36,000
Electricity	1.42×10^6 kWh	$0.02/kWh	28,400
Maintenance @ 5% of Investment			16,600
TOTAL VARIABLE COSTS			$ 81,000
Fixed Costs			
Capital Recovery (10 yrs @ 10%)			53,400
Taxes and Insurance (2% of Investment)			6,660
TOTAL FIXED COSTS			60,000
TOTAL ANNUAL COSTS			$141,000
Unit Cost, ¢/1000 gal			48.3
Unit Cost, ¢/lb phenol removed			$161

Source: Arthur D. Little, Inc., estimates.

The stream characteristics and ozone requirements we have assumed are:

stream flow: 800,000 gal/day
influent phenol concentration: 0.38 ppm
effluent phenol concentration: 0.012 ppm
ozone dosage: 20-40 ppm
ozone generator output: 190 lb O_3/day

These parameters correspond to those given in the literature (Ref. 5) for a Canadian oil refinery.

The operating cost is estimated to be 48¢/1000 gal. This is a rather nigh unit cost for a waste treatment process, especially when one considers that only 2.4 lb/day of phenol is being removed. One reason for the high cost is that treatment must be sufficient to meet an effluent standard of less than 15 ppb of phenols. Another reason is that there are species other than phenol present that exert ozone demand.

A similar unit cost has been estimated for ozonation of a cyanide-containing plating waste. In that case, the capital cost of treating 100,000 gallons/day to reduce CN^- from 50 ppm to 0 was estimated as \$50,000. The operating cost, including electricity, maintenance and labor, was estimated at \$0.45/1000 gal or \$45/day.

Both of these processes have relatively low total ozone demand (ca 200 lb/day), and use fairly high ozone dosages (20-40 ppm for the refinery and 400 ppm for the cyanide process). The unit cost per 1000 gallons will go down as the total ozone demand goes up, because of the reduced cost per pound of ozone-generating equipment, and as the ozone dosage decreases. Labor and maintenance requirements will not be substantially increased even in much larger facilities, since systems are fully automatic. For very large installations, power costs can be reduced by a factor of two and the overall cost reduced substantially, by using oxygen instead of air for the ozonizer feed.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

A. BENEFITS AND LIMITATIONS OF THE PROCESS

1. Ozonation is suitable for streams with a low concentration of oxidizable material. Such dilute streams are most difficult to treat by bulk removal processes such as solvent extraction or precipitation.

2. Technology for large-scale generation and application of ozone to aqueous and gaseous streams is well developed.

3. Ozone has been demonstrated as effective in a number of hazardous waste applications.

4. Ozonation systems are relatively capital-intensive. Operating costs are not especially high and consist mainly of the cost of power for ozone generation.

5. Ozone treatment is likely to be cost-effective when compared to other advanced treatment processes, such as activated carbon adsorption, which are viable alternatives for similar wastes.

6. Energy requirements for ozone generation are substantial, but may be no more than those for competitive processes.

7. The pollution potential of the process will vary with the particular application, but is not excessively high.

8. Provided that excess ozone itself is not allowed to escape, ozonation produces no inherent hazardous emissions in either the gaseous or the liquid effluent streams.

B. PROJECTED IMPROVEMENTS IN EQUIPMENT

Improvement in ozonation process efficiency appears to be probable within the next few years in the following areas:

1. **UV/ozonolysis**

   Houston Research, Inc. has done numerous studies which indicate that the efficacy of ozone treatment can be improved by the incorporation of UV lamps in the ozonation system. The UV-catalysis also serves to make previously resistant compounds susceptible to ozonation (Ref. 1).

2. Contact Systems

It appears that efficiency of ozone utilization (percentage of ozone supplied by the generator that goes into solution and is available for waste component oxidation) is the parameter most amenable to short-term improvement.

Some improvements, such as combinations of ultrasonics with ozonation, may not be economically feasible because the additional energy costs for the ultrasonics exceed energy benefits from reduced ozone demand. Advances in the design of ozone-waste contact systems are, nonetheless, feasible.

3. Ozone Generators

Both major ozone equipment manufacturers and various entrepreneurs are seeking a system which will generate ozone in high concentration at lower electrical cost.

One proposed system is an electron-beam ozone generator which is expected by the developers, RP Industries of Hudson, Mass., and Accelerators, Inc., of Austin, Texas, to produce 50 lb (23 kg) O_3/hr per generator unit at an electrical cost of <1kWh/lb O_3. This device is expected to tolerate ambient humidity levels in the air feedstock. If the device can in fact be scaled up from the presently obtainable level of 0.15 oz O_3/hr to the anticipated outputs, the new ozone generator could produce significant savings in the cost of ozonation. At the ozone levels now obtainable, the energy requirement for ozone generation is <1kWh/lb O_3.

Other experts in the mainstream of corona-discharge ozone generators, the only system proved practical to date for large-scale ozone production, predict substantial improvements in ozonator design and performance. It is not impractical, according to one such expert, to expect that within 5 years ozone generators of the corona-discharge type will produce 5% ozone by weight of wet air at 1 kWh/lb O_3.

These developments would obviously expand the concentration range of streams that could be treated and increase the efficiency of treatment of streams presently treatable.

C. RECOMMENDATIONS

1. General Studies

a. A more exhaustive study should be made of the literature references on susceptibility of various species to ozonation.

b. Laboratory studies should be conducted using carefully controlled conditions to evaluate the effectiveness of ozone treatment of various pollutants of current concern. These studies should evaluate the distribution of products formed, as well as the decrease in concentration of original species.

c. Additional support should be given to research and development aimed at more efficient ozone generation and at improved ozone/water mixing.

2. Specific Wastes

a. Ozone should receive serious consideration for sole or final treatment of any aqueous or gaseous stream containing $<1\%$ of oxidizable hazardous component.

b. In particular, ozonation should be considered as a treatment for streams containing low levels of components for which very stringent effluent guidelines exist (for example, phenols and cyanides).

c. Ozonation should be considered as a preliminary treatment for more concentrated wastes which are not amenable to other treatment techniques.

d. Ozonation will be particularly attractive in situations where an existing treatment process produces a dilute effluent which is fairly dilute in oxidizable hazardous component(s), but which does not meet present effluent standards.

e. Ozonation has a special advantage for wastes which are to be discharged to natural waters because of the high D.O. resulting from ozone decomposition.

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PHOTOLYSIS

Prepared by

Judith C. Harris

I. CONCLUSIONS AND RECOMMENDATIONS

Technology for large-scale application of photolysis to wastes is not highly developed. Pure photolysis is not likely to be a practical industrial waste treatment process within the next 5-10 years. Further laboratory studies of photolysis of selected candidate waste streams (for example, pesticide contaminated solvents) should be conducted.

II. PROCESS DESCRIPTION

A. BACKGROUND

Photolysis is a process in which chemical bonds are broken under the influence of light. In the primary photochemical process, the target species is converted to an electronically excited state, usually a di-radical, which is sufficiently energetic to undergo chemical reaction. The fate of the excited molecule, and therefore the effectiveness of a photolysis treatment process, will depend on its chemical structure and on the medium in which the reaction is carried out.

In order that a proposed photolysis process be effective in treatment of an industrial waste stream, the following criteria must be met:

1) The radiation source must be sufficiently energetic to produce electronic transitions.

2) The radiation must be absorbed by the target species.

3) The ultimate photochemical products must be less toxic than the original stream component.

B. UNDERLYING PRINCIPLES AND OPERATING CHARACTERISTICS

1. Radiation Sources

Covalent bond energies are typically of the order of 50-150 Kcal/mole. In order to cause bond breakage, electromagnetic radiation must be of comparable energy. This requires visible (λ = 750 to 400 nm, E = 38 to 71 Kcal/mole) or ultraviolet (λ = 400 to 200 nm, E = 71 to 143 Kcal/mole) light. (Far ultraviolet radiation would also be effective, but air is opaque to wavelengths less than about 200 nm.) Sources of radiation in this portion of the spectrum include:

a) Sunlight

Solar radiation at the earth's surface is perfectly capable of initiating photochemical reactions (photosynthesis, sunburn, fading of dyes, etc.). A number of studies have shown that natural illumination can cause photodecomposition of pesticides and other contaminants in the environment. In general, however, sunlight is not sufficiently intense to serve as a UV-visible source for waste treatment.

b) Fluorescent Lamps

Ordinary fluorescent lamps can be used quite successfully to simulate solar radiation. These tubes have been used extensively in laboratory studies on the fate of chemicals in the environment. Again, however, the intensity of high energy radiation is low.

c) Low Pressure Mercury Arc

Low pressure mercury arcs (e.g., Germicidal lamps) have two primary emission bands centered at 253.6 and 184.9 nm (112 and 154 Kcal/mole). If advantage is to be taken of the shorter wavelength band, the lamp must be made of quartz, as glass is opaque to this radiation. The total UV output ($\lambda <$ 380 nm) of a low pressure lamp is roughly 2.5 watts per foot of arc length. This may suffice for a treatment process if the target compound absorbs strongly at one of the lamp emission maxima.

d) Medium Pressure Mercury Arc

A medium pressure mercury arc is about 100 times as intense as the low pressure tube; total UV output is on the order of 220 watts per foot of arc length. The wavelengths of maximum emission are different as well. Usable intensities are found at 578 nm (yellow), 546 (green), 436 (blue), 405-408 (violet) and, in the UV, 365, 334, 313, 300, 280, 265, 253, and 238 nm. Both because of the higher intensity and because of the greater range of frequencies emitted, these lamps are potentially of much greater utility for waste treatment.

e) High Pressure Mercury Arc

The high pressure arc is about 10 times more intense than the medium pressure source. The emission is almost continuous in the 265-291 nm range. Lamp output is not as stable or reproducible as in the lower pressure lamps, but this is not a major disadvantage for a waste treatment application. One disadvantage of these lamps is that the useful arc life is only about 75 hours compared to 1000 hours for medium and 12,000 hours for low pressure arcs. The high pressure arc may, nevertheless, be the only sufficiently intense source for some applications.

2. Absorption of Radiation

In order for photolysis to occur, the radiation must be absorbed by (or transferred to, in the special case of sensitized reactions) the target molecule. There are, therefore, two constraints on the type of waste stream suitable for photolytic treatment. One has to do with the hazardous component(s) *per se* and the other with the nature of the stream.

a. Hazardous Component

Photolytic decomposition will not occur unless the target component has an absorption maximum which corresponds to an emission band of the radiation source. Both the wavelength of maximum absorption and the intensity of the absorption are dependent on molecular structure. The wavelength of maximum absorption, λ_{max}, is inversely related to the energy difference, ΔE, involved in the electronic transition from the ground state to the electronic state of the target species:

$$\lambda_{max} = hc/\Delta E$$

where h is Planck's constant and c is the speed of light. A convenient measure of absorption intensity is the absorbtivity, ϵ, which is defined by the Beer-Lambert law:

$$A = \log \frac{I_o}{I} \epsilon C \ell$$

where A is the absorbance, I_o and I are the intensities of the incident and transmitted light beams, C is the (molar) concentration, and ℓ as the path length through the sample.

Some examples of λ_{max} and ϵ_{max} values are given in Table 1. Saturated hydrocarbons, simple alcohols and ethers, and most inorganic species have weak absorptions at very short wavelengths and are, thus, not good candidates for photolysis. Simple organic acids, aldehydes, ketones and halides also have very weak absorptions in the UV-visible regions. On the other hand, highly conjugated systems, including aromatics, are good potential candidates for photolytic treatment.

b. Waste Stream

The types of waste streams to which photolysis can be applied are limited by the fact that the stream itself must be transparent to the exciting radiation. This means that the process is limited to vapors and to liquid streams with low solid loadings; suspended solids adsorb and scatter the incident radiation so that very little of it reaches the target species. Furthermore, the stream cannot contain appreciable quantities of material, including the target compound, which absorb the exciting radiation. (A stream containing 1% of a component of molecular weight 100 and absorptivity of 1000 would be virtually opaque [$I < 0.1\%$ of I_o] if the pathlength exceeded 0.03 cm!)

TABLE 1

EXAMPLES OF WAVELENGTHS AND INTENSITIES OF MAXIMUM ABSORPTION OF UV-VISIBLE LIGHT

	λ_{max}	ϵ_{max}
Propane	135 nm	
Methanol	183	150
Trimethyl Amine	227	900
Methyl Iodide	258	378
Acetone	166	16,000
	189	900
	279	15
Acetic Acid	208	32
Ethylene	171	15,530
Butadiene	217	20,900
Methyl Vinyl Ketone	213	7,100
	320	27
Benzene	184	47,000
	202	7,000
	255	230
Phenol	211	6,200
	270	1,450
Benzophenone	245	22,700
	345	146

Source: J. R. Dyer, *Applications of Absorption Spectroscopy of Organic Compounds,* Prentice-Hall, Inc., 1965, p. 9.

3. Photochemical Products

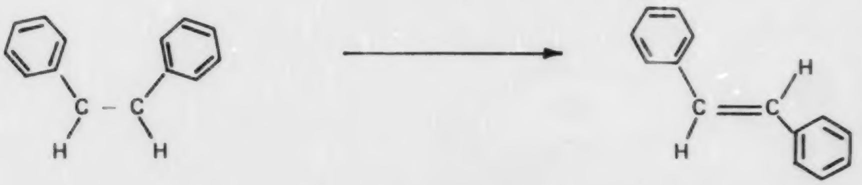
It was noted above that the primary product of the initial photochemical event was usually a di-radical. The further chemical reactions which this species undergoes will determine whether photolysis can, in fact, reduce the hazard level of a particular waste stream.

a. Deactivation

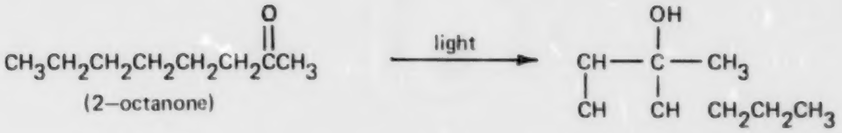
One very probable fate for the electronically excited state is return to the ground state with emission of radiation. Quite obviously, this pathway does nothing to effect treatment of the hazardous waste stream. Photochemical processing will be effective only if uni- or bi-molecular reactions of the di-radical occur at a rate competitive with the deactivation. The extent of radiational deactivation varies with chemical structure and the nature of the medium; it can approach unity. For example, perylene in benzene solution has a fluorescence quantum yield (ratio of photons emitted by fluorescence to photons absorbed) of 0.98. Benzene itself has a fluorescence quantum yield of only 0.04.

b. Molecular Rearrangements

Many organic compounds undergo isomerizations after photoexcitation. For example, cis-stilbene can be converted to the transisomer, and 2-octanone yields 1-methyl-2-propylcyclobutanol. Except in unusual circumstances, it seems unlikely that processes of this type would effect significant detoxification of a hazardous waste stream.



cis-stilbene



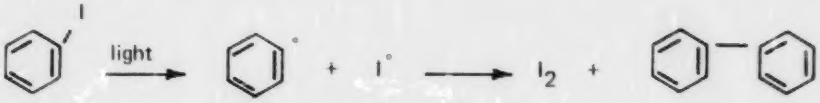
$$CH_3CH_2CH_2CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{light} \begin{array}{ccccc} & & OH & & \\ & & | & & \\ CH & — & C & — & CH_3 \\ | & & | & & \\ CH & & CH & & CH_2CH_2CH_3 \end{array}$$

(2–octanone)

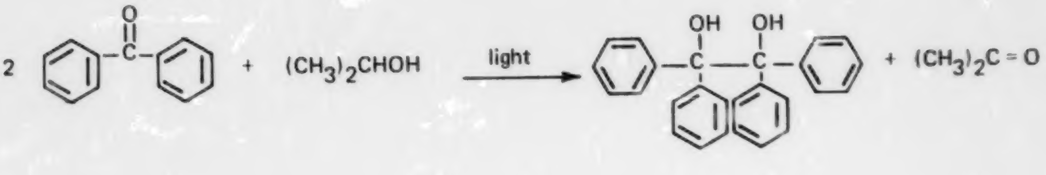
(1–methyl–2–propylcyclobutanol)

c. Fragmentation into Free Radicals

A fairly probable fate of an organic diradical is fragmentation into two free radicals by cleavage of C-C or other bonds. In the absence of other reactants, usual recombination and disproportion reactions occur:



if active hydrogen donors are present, photoreduction products are formed:



If active unsaturated compounds are present, the free radicals may add to them to produce other, larger radicals.

Whether processes such as these can achieve detoxification of a hazardous waste stream obviously depends very strongly on the nature of the original hazardous component(s) and the other species present in the stream. In the examples given above, no significant detoxification would occur.

d. Photo Oxidation

A special application of photolysis in hazardous waste treatment is the use of UV light as a "catalyst" for more conventional oxidation procedures. Two processes of this type are described in Section III.

III. APPLICATIONS TO DATE

We know of no pilot or full-scale applications of a "pure" photochemical process (treatment by UV-visible light alone) to the decontamination of industrial waste streams. Some laboratory studies have been conducted on photolysis in order to predict or explain the behavior of particular compounds when exposed to natural sunlight in the environment. Some pilot scale studies have also been done on the utility of photolytic methods of polishing secondary effluent from waste treatment plants. These studies, however, are not directly relevant to hazardous waste streams.

A. PRINCIPAL CURRENT APPLICATIONS

We have identified two commercial organizations which have direct experience in pilot and full-scale operation of photo oxidation procedures of industrial waste streams.

1. Dow Chemical Company: UV-Chlorination

Dow Chemical, with joint funding from EPA, has developed a UV-chlorination process to remove acetic acid from 200 gpm of a brine stream. The brine is recycled to Dow's chlor-alkali process. The acetic acid is oxidized to CO_2 and CH_3Cl by a combination of Cl_2 and irradiation. High-pressure mercury arcs are immersed in quartz wells in the 12,000 gallon tank, maintained at above ambient temperature. Residence time in the reactor is about 1 hour. This facility has been in use for over a year, and consistently achieves better than 90% acetic acid removal. Cost data show that the process is at least competitive with carbon absorption for acetic acid removal.

2. Houston Research, Inc.: UV-Ozonolysis

Houston Research, Inc., has developed UV-Ozonolysis treatment units for oxidation of refractory materials such as complexed cyanides, organic nitrogen compounds and acetic acid. It is claimed that the addition of UV radiation to the process enhances the reaction with ozone 10^2 to 10^4 fold. A variety of UV sources are used depending on application. Facilities capable of treating 100 gpm have been installed, with removal efficiencies of $> 90\%$. Residence times are 0.5 to 1 hour. Not only the particular hazardous component(s), but the total organic carbon is reduced in concentration; through control of ozone and UV levels, complete conversion to CO_2, H_2O, etc., is claimed.

Cost of installation of a 100 gpm plant are quoted to be $350,000 to $600,000, and operating costs are on the order of $1 to $4 per 1000 gallons.

B. POTENTIAL APPLICATIONS TO WASTE TREATMENT

With the exception of the two processes noted above, no actual applications of photolysis to waste streams have been identified. Because of the nature of the process, however, it is possible to specify potential candidates.

1. Physical Form of Waste

Yes	No
gases	slurries
aqueous solutions	sludges
non-aqueous solutions	tars
clear liquids	

2. Chemical Nature of Contaminants

	Yes	No
Inorganics	cyanides	heavy-metals
	carbonyls	fluorides
		acids
Organics	aromatic hydrocarbons	aliphatic hydrocarbons
	aromatic amines	chlorinated aliphatics
	aromatic alcohols	aliphatic alcohols
	aromatic ethers	aliphatic ethers
	halogenated aromatics	aliphatic amines
	nitro and nitroso compounds	aliphatic acids
	phosphorous and sulfur pesticides	

3. Nature of the Output Stream

In general, the physical form of the output stream would be the same as the input, although some gaseous products may be formed from portions of liquid input streams.

The hazardous component(s) of the stream would be destroyed by photolysis and therefore could not be recovered for reuse. It might well be converted to an innocuous form but would not generally be concentrated or separated.

IV. ENERGY, ENVIRONMENTAL ISSUES, AND ECONOMICS

A. ENERGY REQUIREMENTS

The efficiency of conversion of electricity to UV radiation in any of the mercury arc lamps is about 20%. The efficiency of transfer of UV energy to chemical bonds, and subsequent bond breakage cannot be estimated *a priori*. Energy requirements would be non-trivial but probably not prohibitive.

B. ENVIRONMENTAL IMPACTS

Complete conversion of an organic contaminant to CO_2, H_2O, etc., by a purely photolytic process is not probable. The effluent stream might be suitable for direct discharge, but would probably require further treatment in, e.g., a fume incinerator (gases) or conventional wastewater treatment plant (liquids). Direct recycle of the decontaminated stream to an industrial process is a real possibility.

C. ECONOMICS

There are basically no data on the costs or treatment except those presented in Section III. A great deal would depend on the type of UV-source required for a particular application.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Photolysis as a hazardous waste treatment process is in such an embryonic state that it is difficult to compile a convincing list of advantages and disadvantages. The following comments are based largely on theoretical considerations:

- It will probably not be feasible to devise a "standard" photolysis process applicable to a wide variety of waste streams. On the other hand, there are probably a considerable number of waste streams (e.g., dozens of different pesticide contaminated solvents) which are not suited to other kinds of treatment and for which photolysis is a viable option. Photolytic treatment might, for instance, convert these streams to a form suitable for conventional wastewater treatment.

- It seems unlikely that photolytic treatment processes will be developed to the point of widespread applicability within the next five years. Purely photolytic processes have not yet been applied to hazardous wastes at the pilot or full-scale level. Combined processes (UV/O_3 and UV/Cl_2) are more highly developed.

- Not enough is known about the economics of the process because too few applications have been studied.

- The pollution potential of the process will vary considerably with the particular application. It is not inherently high.

- Depending on the light intensity required, energy requirements may be substantial.

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REDUCTION, CHEMICAL

Prepared by

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I. CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

- Chemical oxidation can detoxify certain hazardous substances.
- Technology for large-scale application of chemical reduction is well developed.
- Application to industrial wastes is well developed for chromium (VI) and for other hazardous species in dilute waste streams (lead and mercury).
- Laboratory and pilot studies have demonstrated potential for reduction treatment of other metals in dilute streams.
- Chemical reduction can, in some cases, process wastes in a way that allows recovery of the metals.
- The major cost of chemical reduction treatment is for the reducing chemicals. The economics vary from one waste to another.
- The equipment required is relatively simple, requiring only storage, metering, mixing, pumping and instrumentation.
- Introduction of foreign ions into the waste is a real or potential disadvantage with many of the reducing agents.

B. RECOMMENDATIONS

- We recommend that chemical reduction be considered for dilute aqueous streams containing the wastes discussed in this report.
- Chemical reduction should be considered as a treatment step when the waste contains chromium (VI).
- Chemical reduction should be evaluated as a preliminary treatment for wastes that have constituents or concentrations of constituents that are not amenable to other treatment methods.
- It should be considered as a final polishing step for traces of contaminants.
- A more exhaustive study should be made of the potential for treatment of hazardous species of current concern. Most of the literature deals only with very dilute wastes and little has been published that is directly relevant to the treatment of concentrated hazardous wastes.

II. PROCESS DESCRIPTION

A. BACKGROUND

Chemical reduction is of interest because metals can often be reduced to their elemental form for potential recycle or can be converted to less toxic oxidation states. One such metal is chromium, which, when present as chromium (VI), is a very toxic material. In the reduced state, chromium (III), the hazards are lessened and the chromium can be precipitated for removal. At the present time, chemical reduction is applied primarily to the control of hexavalent chromium in the plating and tanning industries and to the removal of mercury from caustic/chlorine electrolysis cell effluents.

B. UNDERLYING PRINCIPLES

Reduction-oxidation, or "Redox" reactions are those in which the oxidation state of at least one reactant is raised while that of another is lowered.

In reaction (1)

$$2H_2CrO_4 + 3SO_2 + 3H_2O \rightarrow Cr_2(SO_4)_3 + 5H_2O \qquad (1)$$

the oxidation state of Cr changes from 6^+ to 3^+ (Cr is reduced); the oxidation state of S increases from 2^+ to 3^+ (S is oxidixed). This change of oxidation state implies that an electron was transferred from S to Cr(VI). The decrease in the positive valence (or increase in the negative valence) with reduction takes place simultaneously with oxidation in chemically equivalent ratios. Reduction is used to treat wastes in such a way that the reducing agent lowers the oxidation state of a substance in order to reduce its toxicity, reduce its solubility, or transform it into a form that can be more easily handled.

The base metals are good reducing agents. This is evidenced by the use of iron, aluminum, zinc and sodium compounds for the reduction treatments identified in this study. In addition, sulfur compounds also appear among the more common reducing agents. They appear in Table 1 along with identified applications.

Table 2 lists the more common reduction reactions for chromium (VI) treatment and their reaction products. Reduction reactions for other wastes appear throughout the text.

C. OPERATING CHARACTERISTICS

1. Stream Characteristics

Liquids are the primary waste form treatable by chemical reduction. The most powerful reductants are relatively non-selective; therefore any easily reducible material in the

TABLE 1

WASTE TREATMENT APPLICATIONS OF REDUCTION IDENTIFIED

Waste	Reductant	References
Chromium (VI)	Sulfur dioxide (often flue gas)	6, 7, 13, 10
	Sulfite salts sodium bisulfite sodium metabisulfite sodium hydrosulfite	6, 18
	Ferrous sulfate	
	Waste pickle liquor	16
	Powdered waste iron Powdered waste aluminum Powdered metallic zinc	
Mercury-containing	Sodium borohydride ($NaBH_4$)	21, 17
Tetra-alkyl-lead	Sodium borohydride	8
Silver	Sodium borohydride	

TABLE 2

CONVENTIONAL WASTE TREATMENT REDUCTION REACTIONS

- Cr^{+6} to Cr^{+3} – using sulfur dioxide

$$(1)\quad \underset{\substack{\text{sulfur}\\ \text{dioxide}}}{4SO_2} + \underset{\text{water}}{4H_2O} \rightarrow \underset{\substack{\text{sulfurous}\\ \text{acid}}}{H_2SO_3} + \underset{\substack{\text{chromic}\\ \text{acid}}}{2CrO_3} + 3H_2SO_3 \rightarrow \underset{\substack{\text{chromic}\\ \text{sulfate}}}{Cr_2(SO_4)_3} + 3H_2O$$

- Cr^{+6} to Cr^{+3} – using bisulfites

$$(2)\quad \underset{\substack{\text{chromic}\\ \text{acid}}}{4CrO_3} + \underset{\substack{\text{sodium}\\ \text{bisulfite}}}{6NaHSO_3} + \underset{\substack{\text{sulfuric}\\ \text{acid}}}{3H_2SO_4} \rightarrow \underset{\substack{\text{chromic}\\ \text{sulfate}}}{2Cr_2(SO_4)_3} + \underset{\substack{\text{sodium}\\ \text{sulfate}}}{3Na_2SO_4} + 6H_2O$$

- Cr^{+6} to Cr^{+3} – using ferrous sulfate

$$(3)\quad \underset{\substack{\text{chromic}\\ \text{acid}}}{2CrO_3} + \underset{\substack{\text{ferrous}\\ \text{sulfate}}}{6FeSO_4} + \underset{\substack{\text{sulfuric}\\ \text{acid}}}{6H_2SO_4} \rightarrow \underset{\substack{\text{ferric}\\ \text{sulfate}}}{3Fe_2(SO_4)_3} + \underset{\substack{\text{chromic}\\ \text{sulfate}}}{Cr_2(SO_4)_3} + 6H_2O$$

waste stream will be treated. For example, in reducing heavy metals to remove them from a waste oil, quantities of esters large enough to cause odor problems may also be formed by the reduction.

Gases such as chlorine dioxide and chlorine have been treated by reducing solutions for the small scale disposal of gas in laboratories. For reduction of fluorine, instead of a solution, a scrubber filled with solid bicarbonate, soda lime or granulated carbon is recommended. Reduction has limited application to slurries, tars and sludges, because of the difficulties of achieving intimate contact between the reducing agent and the hazardous constituent. Consequently the reduction process would be very inefficient.

In general, hazardous materials occurring as powders or other solids would usually have to be solubilized prior to chemical reduction.

2. How Process Operates

The first step of the chemical reduction process is usually the adjustment of the pH of the solution to be treated. With sulfur dioxide treatment of chromium (VI), for instance, the reaction requires a pH in the range of 2 to 3. The pH adjustment is done with the appropriate acid, sulfuric, for example. This is followed by the addition of the reducing agent. Mixing is provided to improve contact between the reducing agent and the waste. The agent can be in the form of a gas (sulfur dioxide) or as a solution (sodium borohydride) or perhaps as a finely divided power if there is adequate mixing. Reaction times vary for different wastes, reducing agents, temperatures, pH, and concentration. For commercial-scale operations for treating chromium wastes, reaction times are in the order of minutes. Additional time is usually allowed to ensure complete mixing and reduction. Once reacted, the reduced solution is then generally subjected to some form of treatment to settle or precipitate the reduced material. A treatment for the removal of what remains of the reducing agent may be included. This can be unused reducing agent or the reducing agent in its oxidized state. Unused alkali metal hydrides are decomposed by the addition of a small quantity of acid. The pH of the reaction medium is typically increased so that the reduced material will precipitate out of solution. Filters or clarifiers are often used to improve separation.

3. Output Stream

While some stream components may be added or removed, the output stream from a chemical reduction treatment is not very different from the input stream. Reducing agents such as sodium borohydride and zinc introduce to the reaction mixture ions that are not easily separable from the product streams. The effluent solution is typically acidic and must be neutralized prior to discharge with materials such as hydrated lime, caustic soda, or soda ash.

D. EQUIPMENT AND MATERIALS

Very simple equipment is required for chemical reduction. This includes storage vessels for the reducing agents and perhaps for the wastes, metering equipment for both streams, and contact vessels with agitators to provide suitable contact of reducing agent and waste. Some instrumentation is required to determine the concentration and pH of the waste and the degree of completion of the reduction reaction. The reduction process may be monitored by an oxidation-reduction potential (ORP) electrode. This electrode is generally a piece of noble metal (often platinum) which is exposed to the reaction medium and which produces an EMF output that is empirically relatable to the reaction condition by revealing the ratio of the oxidized and reduced constituents. Figure 1 shows a process flow diagram for a typical chemical system.

Numerous companies have commercial units for the treatment of chromium (VI) in industrial effluents. All of these units offer the user a pre-engineered system for a specific waste or range of waste streams.

The chemical reducing agents that have been identified in this study are commercially available. Their prices are as follows (OPD Chemical Marketing Reporter, April 1976):

sulfur dioxide	6.5¢/lb (in ton containers)
sodium bisulfite	13.4¢/lb
ferrous sulfate	2.6¢/lb
sodium borohydride	$7.50/lb

Since varying amounts of these are required for treatment of a specific waste (because of reducing potential or other characteristics of the chemical), it is not possible to say that the least expensive on a weight basis is the least expensive to treat a specific waste. Additional information is required. Table 3 illustrates how chemical requirements vary for a specific chromium-containing waste.

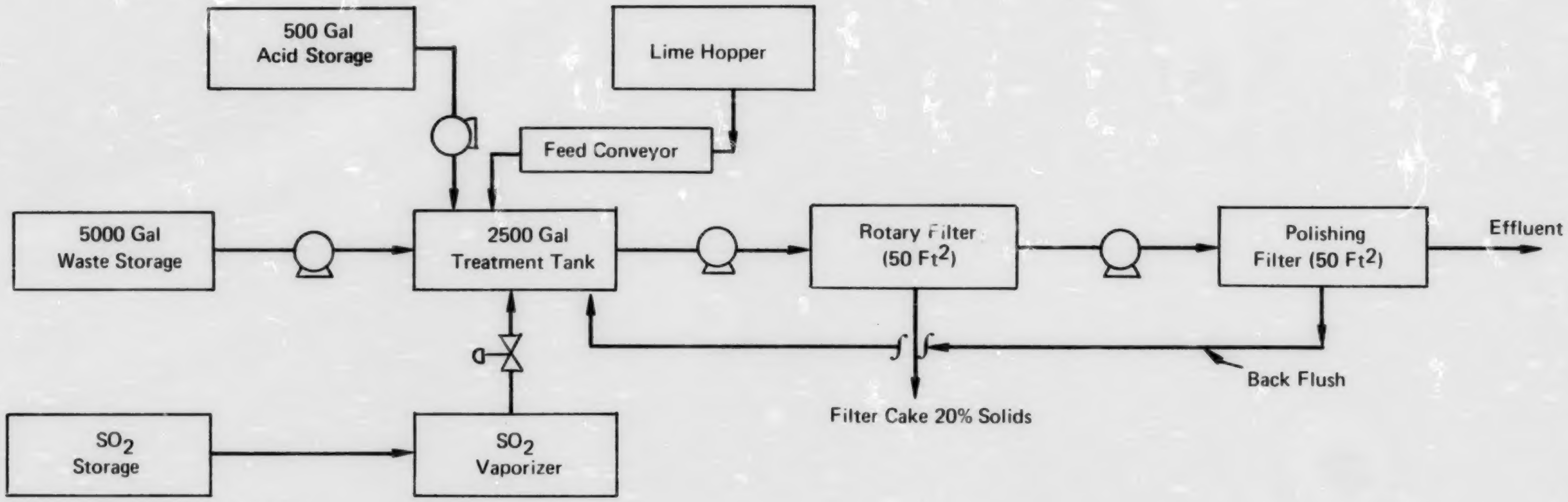
TABLE 3

CHEMICAL CONSUMPTION IN CHROMIUM WASTE TREATMENT

Chemical	Amount Required of Component (lb)
Sulfur dioxide	1.9
Sodium bisulfite	3.0
Sodium metabisulfite	2.8
Ferrous sulfate	8.8

Source: Ref. 6.

In addition to the reducing agent, approximately 1.1 pounds of hydrated lime will be required to neutralize one pound of reduced chromic acid.


500 Gal
Acid Storage
Lime Hopper
Feed Conveyor
5000 Gal
Waste Storage
2500 Gal
Treatment Tank
Rotary Filter
(50 Ft^2)
Polishing
Filter (50 Ft^2)
Effluent
Back Flush
Filter Cake 20% Solids
SO_2
Storage
SO_2
Vaporizer

Treatment: Batch
Waste: Concentrated Chrome Waste
100,000 ppm CrO_3; 85% as Cr^{+3}
In 20% H_2SO_4
Waste Processing Capacity: 2000 Gal/Shift
Operating Period: 240 Days/Yr
8 Hours/Day

Raw Materials:
240 lb/Day SO_2
2065 lb/Day Lime

FIGURE 1 TYPICAL PROCESS FLOWSHEET FOR CHEMICAL REDUCTION

III. APPLICATIONS TO DATE

Reduction reactions are among the most common of chemical reactions. Experience with these reactions for waste treatment is primarily related to removal of trace contaminants in water effluents and for chromium (VI) treatment from operations such as plating and metal finishing. The former are of interest only as they identify potential reducing agents and type of materials that can be reduced. The latter, while often relating to dilute chromium (VI) in rinse wastes, can be extended to more concentrated solutions that have relevance to this contract.

A. PRINCIPAL CURRENT APPLICATIONS

The following paragraphs describe some selected examples of the application of chemical reduction to hazardous waste management problems.

1. Reduction of Chromium (VI) to Chromium (III) in Effluents

Numerous plating and metal finishing plants treat their chromium (VI) wastes using chemical reduction methods. Cyanides and chromium are often present together in plating industry wastes (Ref. 6). The concentrations of these substances and their potential recovery value influence the selection of the treatment process. If the cyanide and chromium are not economically recoverable by a method such as ion exchange, the cyanide radical is first destroyed or converted to the less toxic cyanate by oxidation and the chromium (VI) is converted, by subsequent reduction, to chromium (III), which precipitates and is removed as a sludge.

Hexavalent chromium can be reduced to chromium (III) by a variety of reducing agents including sulfur dioxide, sulfite salts, and ferrous sulfate. In industry the most widely used reducing agent for this purpose is sulfur dioxide. Because soluble chromium (III) compounds are themselves toxic, chromium reduction processes are usually followed by a precipitation operation in which the chromium (III) is precipitated as $Cr(OH)_3$ with either lime or sodium carbonate. In the tanning and plating industries, sludges containing from 10-80% solids obtained from prior concentration of chromates are often redissolved by acidification and then subjected to reduction followed by precipitation to obtain the chromium in an insoluble, concentrated form.

a. Reduction Using Sulfur Dioxide

Figure 1 in the preceding section presents a schematic flow diagram for chromium waste treatment using sulfur dioxide. The reaction equations are as follows:

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$2H_2CrO_4 + 3H_2SO_3 \rightarrow Cr_2(SO_4)_3 + 5H_2O$$

Using hydrated lime the neutralization is:

$$Cr_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Cr(OH)_3 + 3CaSO_4$$

Hexavalent chromium can be reduced to the range of 0.7 to 1 mg/l in the effluent by using such a treatment including reduction, chemical precipitation and sedimentation (Ref. 30).

b. Reduction With Sodium Metabisulfite (and Bisulfite)

About three pounds of sodium metabisulfite ($Na_2S_2O_2$) are required to reduce one pound of hexavalent chromium.

$$4H_2CrO_4 + 3Na_2S_2O_5 + 3H_2O + 6H_2SO_4 \rightarrow 2Cr_2(SO_4)_3 + 6NaHSO_4 + 10H_2O$$

c. Reduction With Ferrous Sulfate

Because of the sludge volume produced, this use of ferrous sulfate is rare in larger-scale treatment facilities.

$$2H_2CrO_4 + 6FeSO_4 + 7H_2O + 6H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 50H_2O$$

2. Removal of Mercury from Effluents

Reduction/precipitation processes are being used increasingly to treat wastewater containing mercury when the flowrate is relatively small and intermittent. Because of its value, and because it is not amenable to disposal, the elemental mercury produced by reduction processes is usually recovered for recycle. Depending upon the process, a cyclone, filter or perhaps a furnace and mercury condenser may be used.

In a reduction/precipitation process which has recently been commercialized, a caustic solution of sodium borohydride ($NaBH_4$) is mixed with mercury-containing wastewater. The ionic mercury is reduced to metallic mercury which precipitates out of solution. The following reaction occurs:

$$4Hg^{2+} + BH_4^- + 80H^- = 4Hg + B(OH)_4^- + 4H_2O$$

In theory 1.0 pound of sodium borohydride can reduce 21 pounds of mercury. In actual operations this is closer to 10 pounds of mercury.

If the mercury solution is in the form of an organic complex, the driving force of the reduction reaction may not be sufficient to break the complex. In that case, the wastewater must be chlorinated prior to the reduction step in order to break down the metal-organic bond.

This reduction process compares favorably with the sulfide precipitation treatment for mercury removal. It does not have a large volume of waste residue. The efficiency is slightly lower in lab scale tests, however, and the $NaBH_4$ is more costly (Ref. 31). Ventron Corporation holds patents for the use of sodium borohydride for heavy metal removal (Refs. 8, 9, 17, 21). Commercial-scale facilities are listed in the references.

Using other metals to reduce mercury ions tends to merely trade one problem for another. Zinc reduction of mercury, for instance, is accompanied by the presence of zinc ions in the effluent stream; however, the zinc compounds are usually found to be less toxic than mercury compounds.

Figure 2 describes the process steps required for mercury removal.

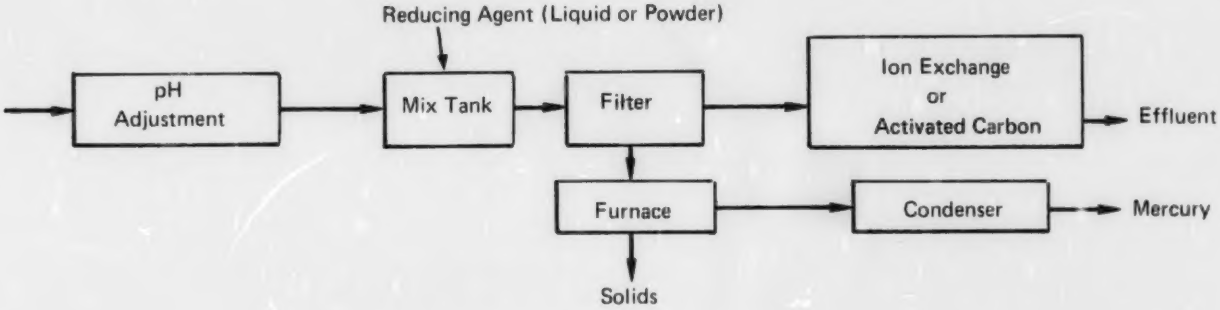

Reducing Agent (Liquid or Powder)
pH Adjustment
Mix Tank
Filter
Ion Exchange or Activated Carbon
Effluent
Furnace
Condenser
Mercury
Solids

FIGURE 2 MERCURY REMOVAL USING CHEMICAL REDUCTION

3. Removal of Lead

a. From Effluents

Removal of dissolved lead compounds, including organo-lead salts, in wastewater from the manufacture of tetra-alkyl-lead compounds is now being done on a commercial scale. The reduction process, using an alkali metal hydride as reductant, lowers the lead content in the waste stream by altering the chemical form of the lead so that it can be precipitated. The reaction is believed to go partially to elemental lead and partially to an alkyl-lead compound that is not stable over long periods of time (Ref. 8), some of which is eventually converted spontaneously to elemental lead. As the element, the lead precipitates and can be removed by techniques such as settling or by filtration.

The concentration range in the effluents to the reduction process are 2-300 ppm. The lead is mostly in the form of soluble organo-lead compounds which will not precipitate with pH adjustment alone, together with some other lead in the form of soluble inorganic lead compounds.

After treatment with an alkali metal hydride [sodium borohydride is preferred in this reaction (Ref. 8)] insoluble lead products are formed. They include hexa-alkyl-di-lead compounds (which may with time decompose to elemental lead), which are formed from the soluble alkyl-lead compounds, and elemental lead from the soluble inorganic lead components.

Low concentrations of the borohydride are preferred because one of the characteristics of the material is that it hydrolyzes with evolution of hydrogen, and with an accompanying loss in its reductive properties. This is particularly true at higher temperatures, pH below 8 or 9, and in the presence of certain catalysts. For this reaction, a pH of 8-11 is preferred.

Table 4 gives information developed in laboratory experiments.

TABLE 4

LAB-SCALE CHEMICAL REDUCTION OF LEAD

Reaction Time (Hours)	Lead Concentration (ppm)	
	Sample A	Sample B
0	8.2	8.2
1	5.8	5.2
2	5.1	4.6
4	3.2	2.6
16	2.4	0.45

Note: Sample A contained 1.0 ppm of sodium borohydride ($NaBH_4$) as the reducing agent. Sample B contained 2.5 ppm $NaBH_4$.

Source: Ref. 8.

b. From Waste Oil

An oil recovery firm has tested the use of a metal hydride for the removal of heavy metals including lead from waste oil by reduction. The product had an odor, probably caused by the production of esters. This was part of a study for the EPA, Contract No. 68-01-0177.

4. Removal of Silver from Effluents

Alkali metal hydride ($NaBH_4$) is being used to recover silver from photographic waste effluents.

5. Removal of Other Metals

Applications are being investigated for the use of sodium borohydride for the removal of trace quantities of other metals from waste streams as either the reduced ion or as the element.

6. Treatment of Inorganic Anions

While not used for waste treatment, the use of $NaBH_4$ for reduction of chlorates (OCl^-) and iodates (IO_3^-) has been studied for analytical purposes.

C. POTENTIAL APPLICATIONS TO WASTE TREATMENT

Chemical reduction should be explored further for the treatment of any of the wastes discussed in the previous section for dilute waste streams. The use of chemical reduction for more concentrated wastes should receive careful evaluation for its comparative economics and the additional pollutant load caused by the addition of chemicals to the waste stream.

The following statements can be made about suitable waste streams:

Physical Form of Waste – Gasesand aqueous solutions are acceptable. Chemical reduction would have limited applicability to slurries and sludges unless it were possible to dilute them for treatment. It might be possible that some waste streams could be contacted for the time necessary, with a sufficient excess of the reducing agent and sufficient mixing to effect treatment. Tars also would find limited applicability.

Chemical Nature of Contaminants – Heavy metals such as chromium, mercury, lead, antimony are removable from waste streams either as the metal hydroxide or the element. Oxidizing agents can be reduced.

Concentration Range – Most of the applications to date have been for dilute systems, generally not more than a few thousand ppm.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Total energy consumption, not including the energy required to produce the chemicals, is low for chemical reduction. The only requirements are for pumping the waste and the reducing agent and for mixing of the two to provide contact.

B. ENVIRONMENTAL IMPACTS

One disadvantage of chemical reduction for waste treatment is that it may introduce new ions into the effluent. If the level of these new contaminants is high enough to exceed effluent regulations, additional treatment operations will be required. Often these are treatments such as precipitation, filtration, or sedimentation.

Air emissions are not expected to be significant from these processes.

After chromium (VI) reduction, the treated solution will be acidic and will also contain the reduced chromium and any other metals present in the original waste stream. Because this solution is corrosive, it may require neutralization prior to discharge or further treatment. Precipitation will occur because of the chemical nature of the materials used and, therefore, settling basins or clarifiers will be required to reduce the solids carry-over.

Small amounts of sulfate resulting from the use of sulfur dioxide on dilute wastes pose no problem, but the zinc ion can be of concern. Reduction with sodium borohydride results in the formation of greater than stoichiometric amounts of soluble borate in the effluent solution; borate at sufficiently high levels could also be of environmental concern. When the waste constituents are present only in very small concentrations these materials in the effluents are of little concern; however, if the processes are extended to more concentrated waste streams additional treatment steps may be needed.

From most of the chemical reductions there will be a residue for disposal unless the concentration of the waste constituent is so low that the reducing agent and the reduced waste can be carried away with the effluent. Residues which eventually will be disposed of on land can be a problem with this treatment process. The sludges formed in follow-up treatment may cause disposal problems because the metal hydroxides they contain may be susceptible to acid leaching. Since the common alkalies used are sodium hydroxide and hydrated lime, a large portion of the sludge will be excess lime and calcium sulfate.

Lesser amounts of waste residues will be produced from the use of sodium borohydride because the metal can often be precipitated in the form of the element or another form that can be processed for recovery.

C. ECONOMIC ANALYSIS

We have prepared a preliminary cost estimate for installation and operation of a facility for the chemical reduction of chromium (VI) waste from a plating operation using sulfur dioxide treatment. The data presented in Table 5 are expressed in 1976 dollars. The stream characteristics and chemical requirements we have assumed are:

Stream Flow: 2000 gallons per day
Treatment: batch
Influent Concentration: 100,000 ppm CrO_3 (85% as Cr^{3+}) in 20% H_2SO_4
Effluent Concentrations: undetectable – Cr^{6+}
Raw Material Dosage
  sulfur dioxide 240 pounds/day
  lime 2065 pounds/day

The operating cost is estimated to be nearly $194 per 1000 gallons. It is difficult to compare this cost with those found in the published literature since other treatment steps such as precipitation are generally considered when presenting the cost of treating wastes such as chromium (VI).

TABLE 5

ESTIMATED OPERATING COST FOR REDUCTION

Basis: Batch Treatment of 2,000 GPD of *Concentrated Chrome* Wastes; 240 days/year

Capital Investment – $230,000

	Annual Quantity	Cost Per Unit Quantity	Annual Cost
Variable Costs			
Operating Labor	2500 MH	$12.00/hr	$ 30,000
Chemicals			
Sulfur Dioxide	29 tons	$170/ton	4,900
Lime	250 tons	$ 35/ton	8,800
Total Chemicals Costs			13,700
Utilities			
Electricity	35,000 kWh	$0.02/kWh	700
Maintenance – (3% Investment)			7,000
Total Variable Costs			51,400
Fixed Costs			
Taxes on Insurance (2% Inv.)			4,600
Capital Recovery (10 yrs @ 10%)			37,000
			41,600
TOTAL ANNUAL COST			$ 93,000
Unit Cost ($/$10^3$ gal)			$193.80

Source: Arthur D. Little, Inc., estimates.

The cost of treatment at individual plant locations and on individual wastes varies greatly. The capital cost will depend upon such factors as type, volume and composition of waste, degree of treatment required, treatment process selected, availability of required services, and whether recovery of metals, chemicals or water is the objective.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

A. BENEFITS AND LIMITATIONS OF THE PROCESS

1. Chemical reduction can often detoxify certain hazardous wastes when the reduced form is either less toxic or more easily removed than the oxidized form.

2. Reduction treatment can, in some cases, process wastes in such a way that allows recovery of the metals.

3. Chemical reduction is suitable for streams with low to moderate concentrations of material which can be reduced.

4. The technology is available and has documented use in industry and for waste treatment (primarily for wastewater treatment).

5. Chemicals are the major portion of the operating costs. As the waste becomes more concentrated this factor may become prohibitive.

6. Chemical reduction is likely to be cost effective for the less concentrated hazardous wastes. Other treatment methods are likely to be more cost effective for other applications (but not exclusively).

7. The equipment used in the process is simple to obtain and use. There is limited use of instrumentation and there are minimal heating and cooling requirements.

8. Energy requirements are not significant.

9. The reducing agents may introduce additional pollutants into the final effluent from the treatment requiring further treatment.

B. PROJECTED IMPROVEMENTS IN EQUIPMENT AND MATERIALS

There are few developments related to equipment and materials that are expected to expand the use of chemical reduction past the current applications. As the problems of hazardous waste disposal become better defined it is expected that new applications for chemical reduction will be developed through additional research.

C. RECOMMENDATIONS

1. General Studies

1. A more exhaustive study should be made on treatability of various waste constituents by chemical reduction.

2. Economic comparisons should be made with the use of other treatment techniques for specific waste streams that are not in the realm of wastewater treatment.

2. Other

1. Chemical reduction should be considered for dilute aqueous streams containing the wastes discussed in this report.
2. Reduction should be considered as a pretreatment for wastes which have constituents or concentrations of constituents which are not amenable to other treatment methods.
3. Chemical reduction should be considered as a final polishing step for traces of contaminants.

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B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD

1. Experts

- Oxymetal Industries, Warren, Michigan (equipment supplier)
- Reuter-Stokes, Inc., Cleveland, Ohio (equipment supplier)
- Ventron Corporation, Beverly, Massachusetts (metal hydride supplier)
- Carlos Lores, Ralph B. Moore; E.I. duPont de Nemours and Co., Wilmington, Del
- Lancy Laboratories, Inc., Zelienople, Pennsylvania
- Battelle Columbus Laboratories, Columbus, Ohio

2. Full Scale Installations Using Process for Industrial Wastes

- Approved Chemical Treatment, Inc.
  Grand Rapids, Michigan
- BioEcology Systems, Inc.
  Grand Prairie, Texas
- Frontier Chemical Waste Process, Inc.
  Niagara Falls, New York
- Nelson Chemicals Company
  Detroit, Michigan
- Silresin Chemical Corporation
  Lowell, Massachusetts
- Western Electric,
  North Andover, Massachusetts
- Boeing Corp.
  Wichita, Kansas
- LTV Corp.,
  Grand Prairie, Texas
- Raytheon Corp.
  Lowell, Massachusetts
- Sobin Chemical Co.
  Orrington, Maine

- Rollins Environmental Services
  Wilmington, Delaware
- Ethyl Corporation
  Pasadena, Texas
- Pontiac Division,
  General Motors Corp.,
  Pontiac, Michigan
- E.I. duPont de Nemours and Co.
  Deepwater, New Jersey
- Processors and Chemical Services, Inc.
  Houston, Texas

3. Facilities that Experimented with the Process for Waste Treatment

- Ethyl Corp.
  Baton Rouge,
  Louisiana
- E.I. duPont de Nemours
  Antioch,
  California
- Eli Lilly Co.
  Indianapolis,
  Indiana

REVERSE OSMOSIS

Prepared by

James D. Birkett

I. CONCLUSIONS AND RECOMMENDATIONS

Reverse osmosis may be used to concentrate dilute solutions of many inorganic and some organic solutes. Preprocessing may be necessary to optimize pH, remove strong oxidants, and filter out suspended solids and film formers. The system is operational at present, with a large number of competitive suppliers.

The system is well worth consideration for treating many streams of soluble organic and inorganic species to produce a concentrate for reuse or disposal and a dilute stream of purified water.

II. PROCESS DESCRIPTION

A. UNDERLYING PRINCIPLES[7, 8, 9, 12]

Reverse osmosis (RO) employs a semipermeable barrier which will pass only certain components of a solution, and a driving force to separate these components at a useful rate. The membrane is permeable to the solvent but impermeable to most dissolved species, both organic and inorganic. The driving force for its separation is an applied pressure gradient.

Conventional "forward" osmosis transfers solvent through a semipermeable separator from more dilute to more concentrated solution, driven by the difference in solvent vapor pressure on either side of the separator. The osmotic pressure π, or magnitude of this driving force, is given by the equation:

$$\pi = \frac{RT}{\nu} \ln \frac{P_1}{P_2}$$

in which R is the gas constant, T is the absolute temperature, ν is the molar volume of the solvent, and P_1 and P_2 are the solvent vapor pressure in the solutions on either side of the membrane. (Note that π is independent of the specific membrane material.)

If a pressure equal to π is applied across the membrane counter to normal solvent flow, no transfer will take place. If a pressure greater than π is applied, solvent will be transferred from the more concentrated to more dilute solution, resulting in both a concentration of solute and purification of solvent. This is reverse osmosis.

The dilute solvent flux, J (frequently expressed in gallons/ft^2-day), is given by:

$$J = K(\Delta P - \pi)$$

in which ΔP is the applied pressure and K is a constant for the membrane-solvent system. As can be seen from this equation, the product-water flux rate decreases with increasing salinity (increasing osmotic pressure) of the feed solution. Thus, the difficulties (and cost) of recovering clean water also increase with increasing salinity of the feed stream. (This principle must be considered when the economics of salt removal from waste streams is calculated; at some point the stream will become sufficiently concentrated to make it more feasible to evaporate the residual brine than to continue reverse osmosis.)

The design of the modules containing the reverse osmosis membranes is crucial to the efficient operation of the process. As solute is rejected by the membranes, it concentrates at the membrane surface and results in a situation known as "concentration polarization," where the concentration at the membrane surface is many times higher than in the bulk feed solution. Since the driving force for water transport (ΔP-π) decreases with increasing concentration, polarization can have a very deleterious effect on water flux.

Concentration polarization can be minimized by high fluid shear at the membrane surface to aid the back-transport of polarized solute into the bulk of the process stream. This is accomplished by flowing the feed stream at high velocities in thin channels to promote laminar shear, or in wide channels to produce turbulence.

The chemical nature of the membrane material is important, because it affects the transport of solvent and rejection of solute. There have been two major hypotheses regarding the functioning of an RO membrane – the pore theory and the diffusion theory. The pore theory suggests that the membrane surface contains pores only a few angstrom units in diameter and molecules are selected for passage on the basis of size. In addition, according to the pore theory a layer of pure water is formed at the membrane surface by the repulsion of ionic species from the surface by their "reflected charge" and this layer of pure water is drawn off through the pores.

The diffusion theory proposes that the surface of the membrane is in fact a thin homogeneous film and that membrane specificity or rejection is the result of widely diffusing permeation rates of solvent and solutes across this layer. The weight of the support has swung to the side of the diffusion theory, on the basis of its ability to correctly predict the effect of changes in pressure and concentration or rejection rates.

Reverse osmosis also differs from "conventional" filtrations in that the flow of the feed is not normal to the membrane surface but tangential to it in an effort to keep it clean of debris and to reduce surface concentration effects. RO membranes do not become "plugged" but they may become fouled by film-forming organics or by insoluble salts and scaling. Much of the prefiltering of the feed water is in fact aimed at preventing the narrow flow channels of the assembled device from becoming plugged.

Cellulose acetate membranes remain the most popular. Ion exchange membranes also produce specific selectivity but are rarely used; polyamide materials, nylons, and polyarylsulfones have recently appeared.[14] Because of the need for high solvent flux rates while withstanding high pressure differentials, most membranes in use today are of the "skinned" type in which membrane casting technique is controlled to produce a very thin homogeneous film or skin upon a more open porous substrate of the same material. (After extended use at high pressures, these may "compact" and lose a significant amount of their permeability.) Typical rejections for a "tight" cellulose acetate membrane are given in Table 1.

B. OPERATING CHARACTERISTICS[10]

Total dissolved solids (TDS) in the feedwater may be as high as that of sea water (34,000 ppm) and product water TDS as low as 5 ppm.

TABLE 1. MEMBRANE REJECTIONS

Salts

CATIONS

Name	Symbol	Percent Rejection	Maximum Concentration Percent
Sodium	Na^{+}	94-96	3-4
Calcium	Ca^{+2}	96-98	*
Magnesium	Mg^{+2}	96-98	*
Potassium	K^{+1}	94-96	3-4
Iron	Fe^{+2}	98-99	*
Manganese	Mn^{+2}	98-99	*
Aluminum	Al^{+3}	99+	5-10
Ammonium	NH_4^{+1}	88-95	3-4
Copper	Cu^{+2}	96-99	8-10
Nickel	Ni^{+2}	97-99	10-12
Strontium	Sr^{+2}	96-99	—
Hardness	Ca and Mg	96-98	*
Cadmium	Cd^{+2}	95-98	8-10
Silver	Ag^{+1}	94-96	*

ANIONS

Name	Symbol	Percent Rejection	Maximum Concentration Percent
Chloride	Cl^{-1}	94-95	3-4
Bicarbonate	HCO_3^{-1}	95-96	5-8
Sulfate	SO_4^{-2}	99+	8-12
Nitrate	NO_3^{-1}	93-96	3-4
Fluoride	F^{-1}	94-96	3-4
Silicate	SiO_2^{-2}	95-97	—
Phosphate	PO_4^{-3}	99+	10-14
Bromide	Br^{-1}	94-96	3-4
Borate	$B_4O_7^{-2}$	35-70**	—
Chromate	CrO_4^{-2}	90-98	8-12
Cyanide	CN^{-1}	90-95**	4-12
Sulfite	SO_3^{-2}	98-99	8-12
Thiosulfate	$S_2O_3^{-2}$	99+	10-14
Ferrocyanide	$Fe(CN)_6^{-3}$	99+	8-14

ORGANICS:

	Molecular Weight		
Sucrose sugar	342	100	25
Lactose sugar	360	100	25
Protein	10,000 Up	100	10-20
Glucose	198	99.9	25
Phenol	94	***	—
Acetic acid	60	***	—
Lactic acid	90	***	—
Dyes	400 to 900	100	—
Biochemical Oxygen Demand	(BOD)	90-99	—
Chemical Oxygen Demand	(COD)	80-95	—
Urea	60	40-60	Reacts similar to a salt
Bacteria & virus	5,000-100,000	100	—
Pyrogen	1000-5000	100	—

GASES, DISSOLVED:

Carbon dioxide	CO_2	30-50%
Oxygen	O_2	Enriched in permeate
Chlorine	Cl_2	30-70%

* Must watch for precipitation, other ion controls maximum concentration.

**Extremely dependent on pH; tends to be an exception to the rule.

***Permeate is enriched in material due to preferential passage through the membrane.

Source: Reference 1.

Cellulose acetate membranes have been the most frequently used in the past, but polysulfones and polyamides (nylon) are increasingly popular for use at high pH values. The hollow fiber type of module has gained rapid acceptance and in terms of total operating units may be the most prevalent.

Because of the susceptibility of the membranes to chemical attack and fouling, and the susceptibility of the flow system to plugging and erosion, it is common to preprocess feed water as necessary to remove oxidizing materials. These include iron and manganese salts, to filter out particulates and, to remove oils, greases, and other film forms. If there is likelihood of fouling by living organisms, chlorination or UV treatment may be employed as well to insure that maximum flux rates may be obtained.

Table 1 indicates typical salt rejection rates for a cellulose acetate membrane. Flux rates (at 400 to 600 psi) range from about 5 to 20 gallons/day/ft^2. Care must be taken that precipitation, and especially scale formation, does not take place on the membrane surface. Water treatment, including chlorination, pH control, and filtering (1-25μ, depending on system) may be required, as discussed earlier.

Most important of all, virtually any potential application must be piloted in order to ensure that its chemistries are well understood and that no unknown factors will arise later.

III. APPLICATIONS TO DATE

A. HISTORY OF USE[1, 2]

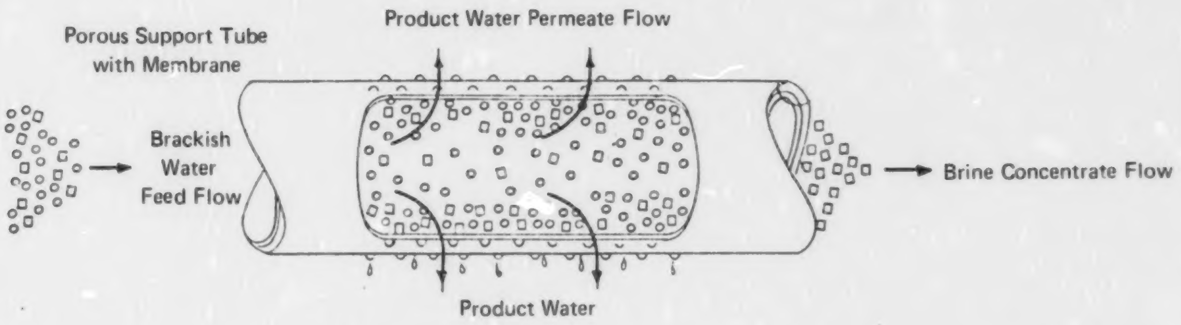
The earliest RO units were constructed in the late 1950's at UCLA, the "birthplace" of reverse osmosis, and at Aerojet General utilizing a plate and frame construction similar to conventional filter presses. Membrane supports were porous stainless steel or bronze. Such a design was suitable for early work but did not allow good enough control of the feed flow to optimize performance. It was also cumbersome and heavy and there were difficulties with maintaining good seals.

About 1961 the tubular design made its appearance, consisting of perforated stainless steel tubes with "liners" of the reverse osmosis membrane having the active or "skinned" side of the membrane facing inwards. Feed was pumped at high pressure through tubes, allowing good control of the flow dynamics. Several tubes could be arranged in a bundle, similar to a tube-and-shell condenser, with the permeate being collected from the shell side. This system performed well but was expensive to fabricate.

Subsequently, Havens Industries introduced a similar but refined system utilizing porous fiberglass tubular supports. While some sealing problems remained, leaks could develop because of the slight solubility of the glass fibers in the pure water permeate; the system was a significant advance and also permitted the use of unfiltered feed water without danger of plugging. In fact, the tubes could be mechanically cleaned if necessary. A typical tubular module is shown in Figure 1.

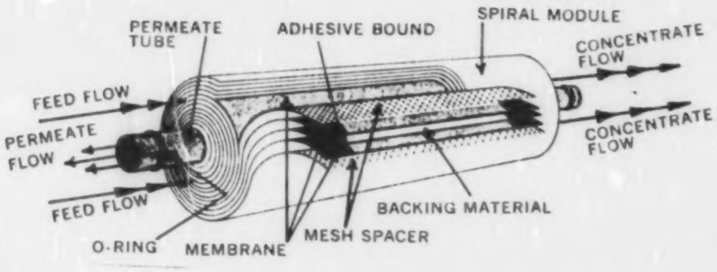
The next design development was that of the spiral-wound cell (largely by Gulf-General Atomic). This design uses envelopes of flat-sheet cellulose acetate or other membrane material wound in a spiral to produce a continuous thin channel through which the feed flows at high laminar shear rates. Spacers of netting maintain optimum distances within and without the envelope and the permeate produced is collected in a perforated mantel to which the envelope is fastened at one end on which it is wound. This configuration is inexpensive, produces high water fluxes, and uses the membrane area efficiently. The membrane and support are in compression and leaks are not a major problem. Although filtration of the feed (to about 25μ) is usually recommended, plugging of the channels is not a major problem. A typical spiral module is shown in Figure 2.

In the last few years a reverse osmosis system using a multitude of hollow nylon or polyamide fibers have shown considerable utility on commercial waste streams and for water purification. DuPont and Dow pioneered this activity. As illustrated in Figure 3, a bundle of fibers, with the "active" side of the nylon membranes on the exterior of the fibers, is encased in a module. (A typical fiber may have an external diameter of $50\text{-}80\mu$ and an internal diameter of $20\text{-}40\mu$). Feed water is passed at high velocities between the fibers, and fresh product water permeates into the interior lumens of the fibers from which it is collected. This configuration results in rather low utilization of membrane area, but, since


Porous Support Tube
with Membrane
Product Water Permeate Flow
Brackish
Water
Feed Flow
Brine Concentrate Flow
Product Water

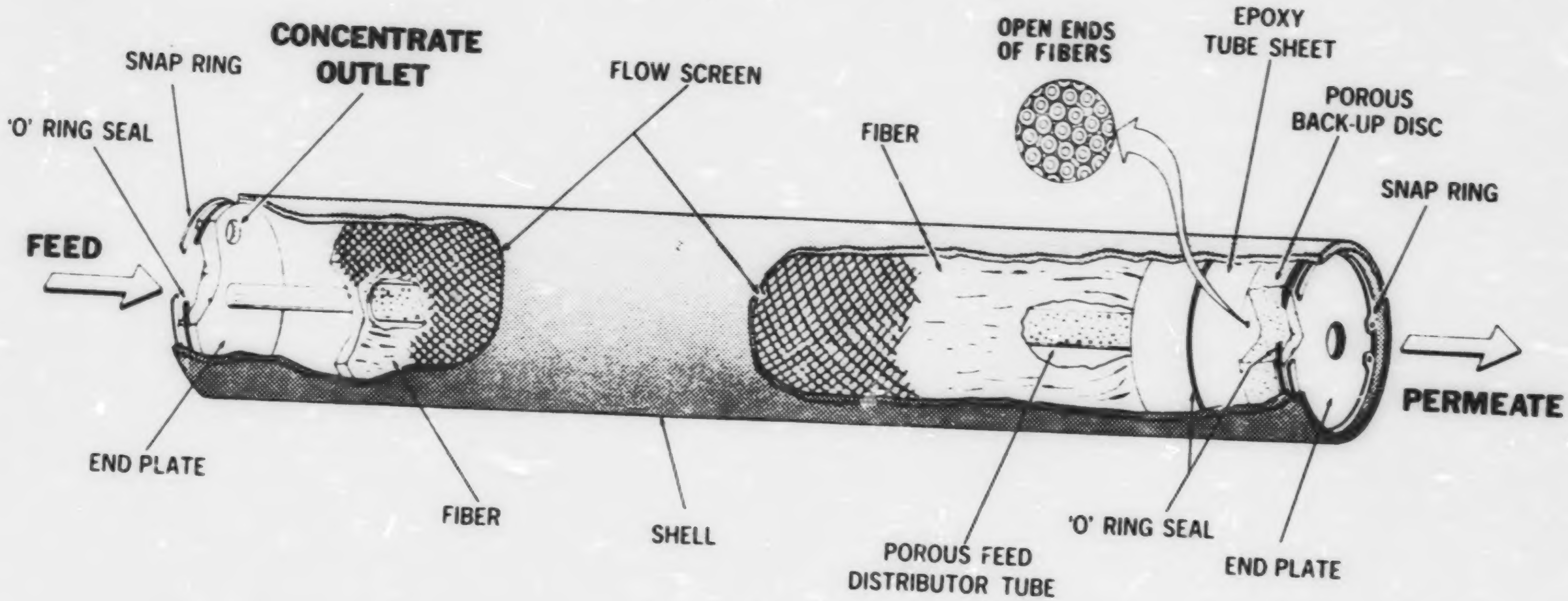
Source: Ref. 1.

FIGURE 1 TUBULAR REVERSE OSMOSIS MODULE


PERMEATE
TUBE
ADHESIVE BOUND
SPIRAL MODULE
CONCENTRATE
FLOW
FEED FLOW
PERMEATE
FLOW
CONCENTRATE
FLOW
FEED FLOW
BACKING MATERIAL
O-RING
MEMBRANE
MESH SPACER

Source: Ref. 1.

FIGURE 2 SPIRAL MEMBRANE MODULE


CONCENTRATE OUTLET
SNAP RING
'O' RING SEAL
FEED
FLOW SCREEN
FIBER
OPEN ENDS OF FIBERS
EPOXY TUBE SHEET
POROUS BACK-UP DISC
SNAP RING
PERMEATE
END PLATE
FIBER
SHELL
POROUS FEED DISTRIBUTOR TUBE
'O' RING SEAL
END PLATE

Source: Ref.17.

FIGURE 3 HOLLOW FIBER MODULE (DUPONT PERMASEP®)

the cost per unit of the membranes is considerably lower than the cost of the cellulose acetate membranes, the ultimate cost of water recovery is competitive for low-salinity feed streams. This configuration is more susceptible to fouling or plugging by suspended solids than the spiral-wound configuration and requires very thorough preprocessing of the feed stream.

One additional design worthy of mention is the "sand-log" tubular system marketed over the last several years by Westinghouse but just recently acquired from them by Union Carbide.[16] This system, shown in Figure 4, is a special form of tubular reverse osmosis in which a resin-bonded porous sand cylinder with a hollow core is encased in a steel pressure jacket. This cylinder serves as the porous support for "active" membrane material which is deposited on the walls of the core. One advantage of the design may be the incompressability of the sand core, which could minimize the degradation of performance. Typical tubular, spiral, and hollow fiber sytems are summarized in Table 2. These represent nearly all of the units in use today. The nylon or amide materials permit operation at high pH values (up to about 11) but are susceptible to oxidation.

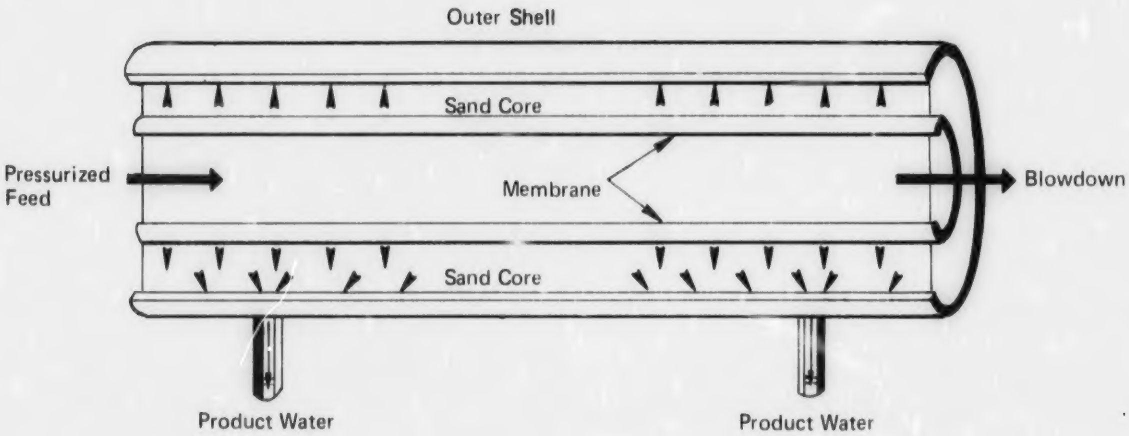
Whichever system is eventually chosen, individual modules are then assembled, as shown in Figure 5, to achieve the desired capacity and degree of separation.

B. PRINCIPAL CURRENT APPLICATIONS[6, 13, 15]

In the past 15 years, reverse osmosis has developed into a technology that is used widely in chemical processing and in the production of fresh water. (In fact, much of the early research and development work was supported by the U.S. Department of the Interior, Office of Saline Water.) At the beginning of 1975 nearly 300 large (> 25,000 gpd) plants were reported in operation around the world producing a total of 45 million gallons per day of purified water for municipal or commercial use from the sea or brackish sources.[3]

The number of plants in use to treat industrial process streams is more difficult to ascertain but, if not comparable, is at least very signicant. Specific applications include the preparation of pure water and process feed water, preparation of rinsewater for use in semiconductor and electronic manufacturing (a major application), purification of water for hospital use, reclamation of electroplating chemicals and water, and recovery of sugar wastes by candy manufacturers.

Present full-scale waste treatment is operational in the electroplating and related industries to process rinse waters that not only have metal salt concentrations which are not legally "dischargeable," but which represent significant expense because of lost chemicals. Reverse osmosis may successfully avoid the dumping problem and provides clean water and concentrated chemicals solutions for reuse. (In fact in such cases, the economic benefits of


Outer Shell
Sand Core
Pressurized Feed
Membrane
Blowdown
Sand Core
Product Water
Product Water

Source: Ref. 16.

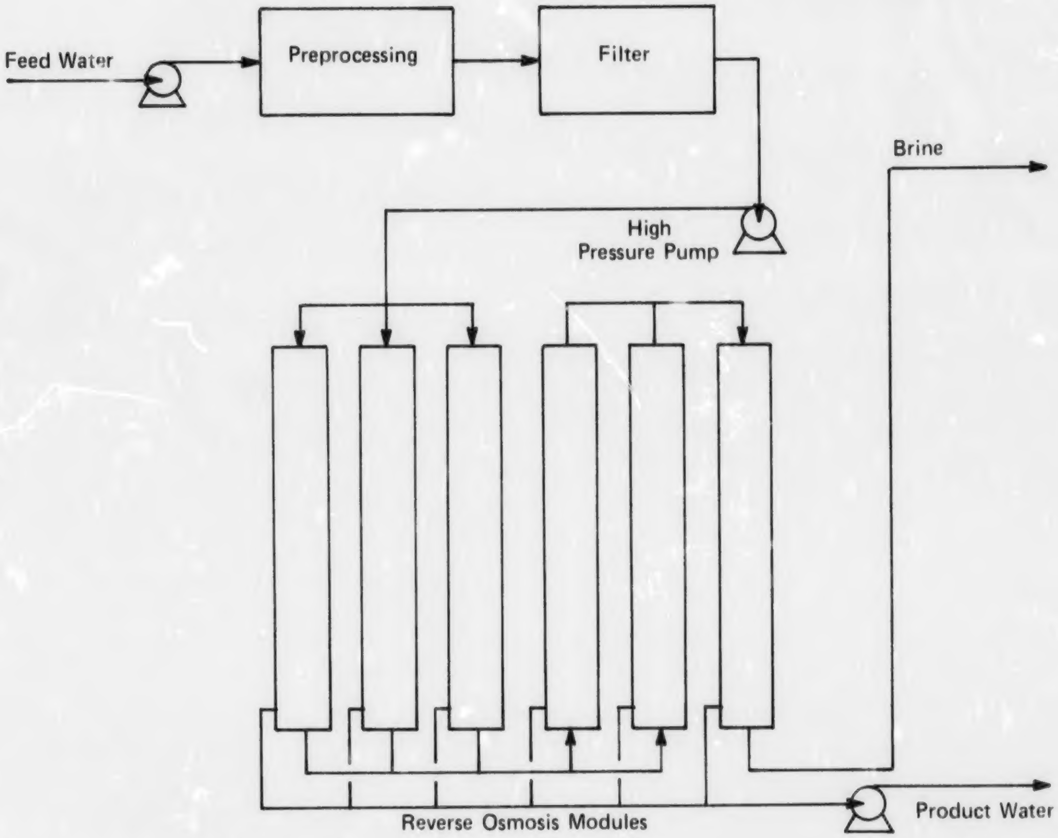
FIGURE 4 SAND-CORE TYPE OF REVERSE OSMOSIS MODULE

TABLE 2

COMPARISON OF REVERSE OSMOSIS MODULE CONFIGURATIONS

	Spiral Wrap	Tubular	Hollow Fine Fiber
Membrane Surface Area per Volume, ft^2/ft^3	100 - 300	40 - 100	5,000 - 10,000
Product Water Flux, gpd	8 - 25	8 - 25	0.1 - 2
Typical Module Factors			
Brine Velocity, ft/sec	0.7	1.5	0.04
Brine Channel Diameter, in.	0.05	0.5	0.004
Method of Membrane Replacement	As a membrane module assembly - on site	As tubes, on site	As entire pressure module on site, module returned to factory
Membrane Replacement Labor	Medium	High	Medium, requires equipment
High Pressure Limitation	Membrane compaction	Membrane compaction	Fiber collapse
Pressure Drop, Product Water Side	Medium	Low	High
Pressure Drop, Feed to Brine Exit	Medium	High	Low
Concentration Polarization Problem	Medium	High	Low
Membrane Cleaning - Mechanical	No	Yes	No
- Chemical	Yes - pH and solvent limited	Yes - pH and solvent limited	Yes - less restricted
Particulate in Feed	Filtration required	No problem	Filtration required
Permissible Feed Ranges, pH	5.5 - 7.5	5.5 - 7.5	2 - 10
Permissible Temperature, ^{o}F	100	100	100

Source: Reference 1


Feed Water
Preprocessing
Filter
Brine
High
Pressure Pump
Product Water
Reverse Osmosis Modules

Source: Ref. 1.

FIGURE 5 REVERSE OSMOSIS PLANT FLOWSHEET

reuse may become sufficiently large that the user may no longer perceive the process as a form of waste treatment.) A limited number of other full-scale uses are found in the paper industry (sulfite streams), in food processing, and in other processing plants. RO is beginning to appear in designs for cooling tower systems to prevent salt build-up in the system and to concentrate that salt for eventual disposal.

C. POTENTIAL APPLICATIONS TO INDUSTRIAL WASTE TREATMENT

In general, reverse osmosis may be considered whenever one must concentrate a waste stream that contains dissolved salts or organic materials to permit their reuse or to reduce the volume of the waste stream prior to evaporation or other disposal.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Power requirements for reverse osmosis are generally about 10 kWh/1000 gallons of product water. Energy savings have been sought by reducing the concentrated brine to atmospheric pressure through a hydaulic turbine but this is generally not practical. In specific instances the feed solution may be at an elevated temperature. If the RO system can be designed by choice of membrane material to operate at this elevated temperature and to return a hot permeate stream to the plant for re-use, there may be some energy savings overall.

B. ENVIRONMENTAL ISSUES

There is no air or solids pollution from a reverse osmosis plant and the only liquid pollution hazard is the concentrated brine or solute solution, which may be recycled or else disposed of in an acceptable manner.

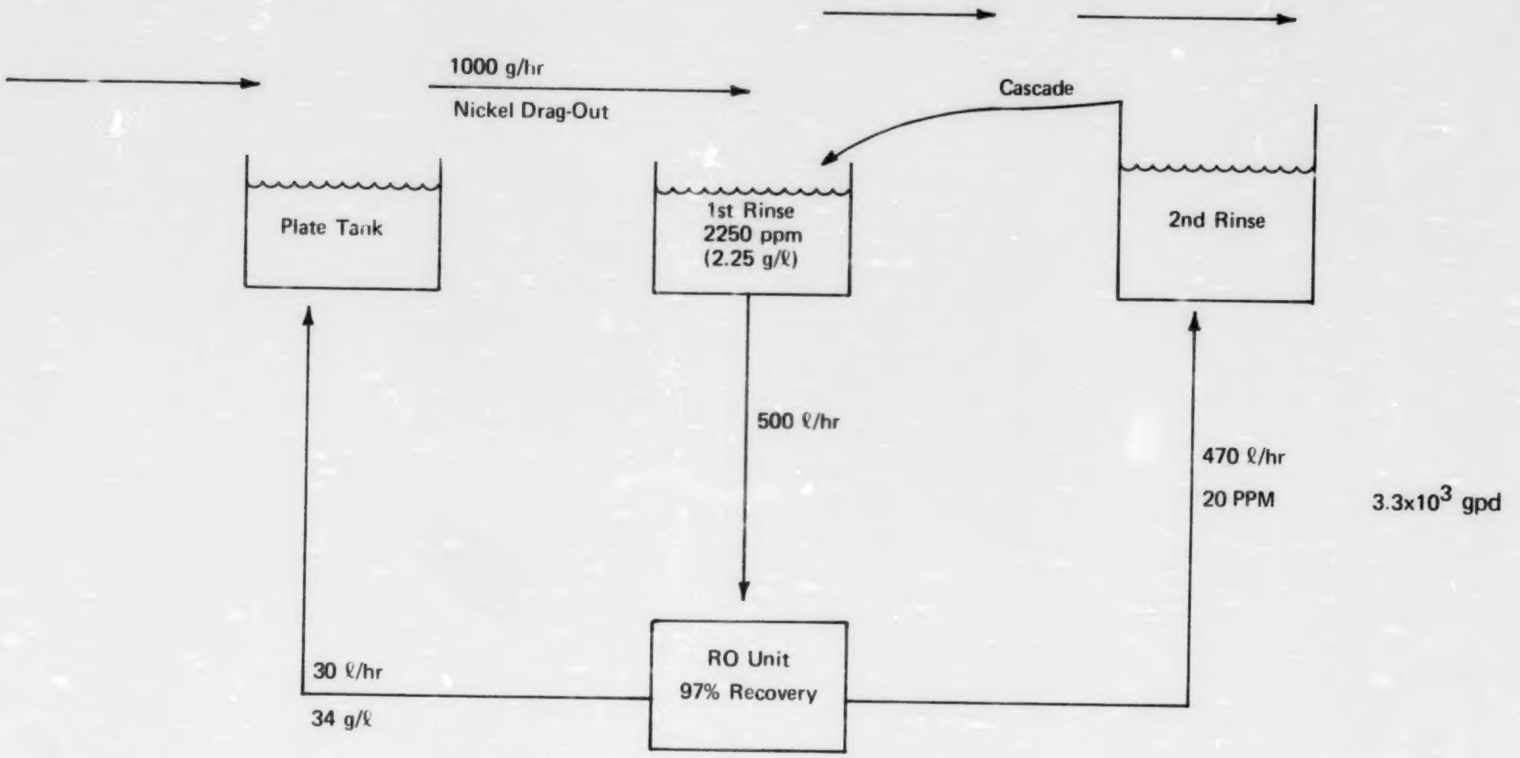
C. ECONOMIC ANALYSIS[5, 11]

Costs of reverse osmosis plants are strong functions of the purified-water output capacity, because this is the material actually *removed* from the feed. (The solutes remain in the feed, which becomes more concentrated.) Construction costs are estimated to range from $800,000 for a 1 million gpd plant to $5 million for a 10-million gpd plant (independent of land and special preprocessing costs).

Smaller plants are obviously more expensive per unit of throughput; the costs of course depend strongly upon the treatment and the final choice of unit. A very small unit, about 500 gallons per day, with high salt rejection might cost as much as $2,000 ($4 per gpd) while a 15,000-gpd unit could cost only $12,000-15,000 ($0.80-$1.00 per gpd).

Direct operating costs vary considerably with the model chosen, but are usually about $0.50/1,000 gallons for large plants, exclusive of cost of capital. About one-third to one-half of the direct operating cost is in the cost of replacement membranes, depending on service conditions. Replacement costs for high-pressure pumps may also be significant.

As an example of the cost of reverse osmosis in a plant of modest size, we have used as a model the nickel plating rinse line illustrated in Figure 6. Such a unit, using cellulose acetate membranes in a spiral configuration might be built and operated at costs such as those shown in Table 3.


1000 g/hr
Nickel Drag-Out
Cascade
Plate Tank
1st Rinse
2250 ppm
(2.25 g/ℓ)
2nd Rinse
500 ℓ/hr
470 ℓ/hr
20 PPM
3.3x10³ gpd
RO Unit
97% Recovery
30 ℓ/hr
34 g/ℓ

*Assume liquid volume of drag-in equals drag-out.

FIGURE 6 RO UNIT FOR USE ON CASCADED RINSES OF ACID NICKEL PLATING LINE*

TABLE 3

ESTIMATED RO PLANT COSTS

Capital Costs (including pumps, filter)	$12,000
Operation Costs per Day	
Electricity (at 2¢/kWh)	0.65
Membrane Replacement (@ 2.5 yrs)	0.95
Labor and Maintenance (1/4 hr @ $12/hr)	3.00
Total Direct Costs per Day	$ 4.60 ($1.40/1000 gal)
Capital Costs (@ 10 yrs, 10% – 330 days per year operating)	5.90 ($1.80/1000 gal)
Total Costs Per Day	$ 10.50 ($3.20/1000 gal)

Source: Arthur D. Little, Inc., estimates

However, this cost must be balanced against the savings in nickel salts (about 50 pounds per day) and lower water costs (about 3000 gallons per day returned to second rinse and cascade). It is also obvious that the figure given for direct labor is a bit artificial; it is too small to be known with accuracy but has strong leverage on the total direct cost.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Use of reverse osmosis in the treatment of industrial wastes is growing rapidly and can be expected to show continued growth as its utility is demonstrated and the technology becomes more familiar to potential users. Thus far the system has not been used to concentrate wastes in nonaqueous solvent streams but in theory this could be done as well if the need were to arise and if the solvent were compatible with its membrane material.

Laboratory work continues at most of the major suppliers, largely aimed at developing membrane materials which will be less prone to fouling and chemical degradation and which will have high water flux rates while still showing good solute rejection characteristics. Longer life at higher temperature, pressure, and pH's is also sought.

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B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD[4]

In the early days of reverse osmosis the industry names most often mentioned were Aerojet-General, Havens, Gulf-General Atomic, Eastman (for membranes), Dow and DuPont (the latter two for hollow-fiber technology). Presently the major module/system manufacturers are UOP (the eventual recipients of the Gulf technology and Havens Industries), Dow and DuPont (major suppliers of hollow-fiber modules, the latter under its registered trade name "Permasep"), Union Carbide (now having acquired the Westinghouse system), Osmonics (using membrane technology developed by Eastman). There are many suppliers of complete RO systems based upon modules supplied by others; the major ones include Abcor (hollow fibers from DuPont and tubular and spiral units from UOP), Permutit (DuPont hollow fiber), El Paso Environmental (UOP spiral), Continental, Ajax, and Polymerics.

STEAM DISTILLATION

Prepared by

Lawrence R. Woodland

I. CONCLUSIONS AND RECOMMENDATIONS

Steam distillation is a proven process for removing water-immiscible, volatile (organic chemical) compounds from process or waste streams. It is also used, in special cases, to recover heat sensitive high boiling water soluble components from waste or process streams.

The process can be applied to any waste stream that can be adequately contacted with steam or water and that does not react or decompose in the presence of water or steam. The waste stream can be in the form of:

- liquids
- slurries
- sludges
- solids

The types of volatile components that can be removed from a process or waste stream include:

Water Immiscible Hydrocarbons – aliphatic
– aromatic

Water Immiscible Halogenated Hydrocarbons

Water Soluble Hydrocarbons (Distilled as Azeotropes) – phenol
– aniline

Water Soluble Hydrocarbons (Non-Azeotrope) – glycerine

II. PROCESS DESCRIPTION

A. BACKGROUND

Steam distillation offers a simple solution to several difficult industrial distillation problems. These include distillations of:

- compounds with relatively high boiling points such as glycerine or lubricating oils
- compounds that may decompose at their atmospheric boiling points such as fatty acids
- chemicals that pose hazardous conditions when distilled without water vapor (steam) present.

One of the earliest forms of steam distillation (although the basic principle was not understood at the time) was the steam distillation of delicate essential oils from flowers, leaves, bark, etc., in perfumery. Later in the early 1900's turpentine was recovered from pine gum, and camphor was obtained from chipped cinamomum camphora by steam distillation. Steam distillation is presently used in the petroleum, coal-chemical, wood chemical, petrochemical, and paper industries. In some cases, steam distillation has been supplanted by vacuum distillation as a means of conducting distillations at lower temperatures (under a lower pressure), while in yet other cases (i.e., petroleum fractionation) a combination of steam and vacuum distillation is used. A choice between vacuum and steam distillation is generally dictated by economics, product purity requirements, and the potential for chemical side reactions with the steam or water.

B. BASIC PRINCIPLES OF STEAM DISTILLATION

With a few notable exceptions, such as steam distillation of glycerine (to prevent degradation), steam distillation generally takes advantage of the unique vapor pressure relationship of two immiscible liquids. That is, each immiscible liquid exerts its own vapor pressure independently, and the total pressure in the distillation system is equal to the sum of the two independent vapor pressures. (In conventional distillation of miscible components, the vapor pressure of each of the components is reduced to its mole fraction in the liquid phase.)

Figure 1 demonstrates the effect of the presence of water or steam on the vapor pressure (boiling point) of toluene.

Without water present, the boiling point at one atmosphere would be 110-111°C, but with a water phase present in steam distillation, the boiling point at 1 atm. (760mm Hg) would only be 84°C. The presence of water lowers the boiling point allowing lower

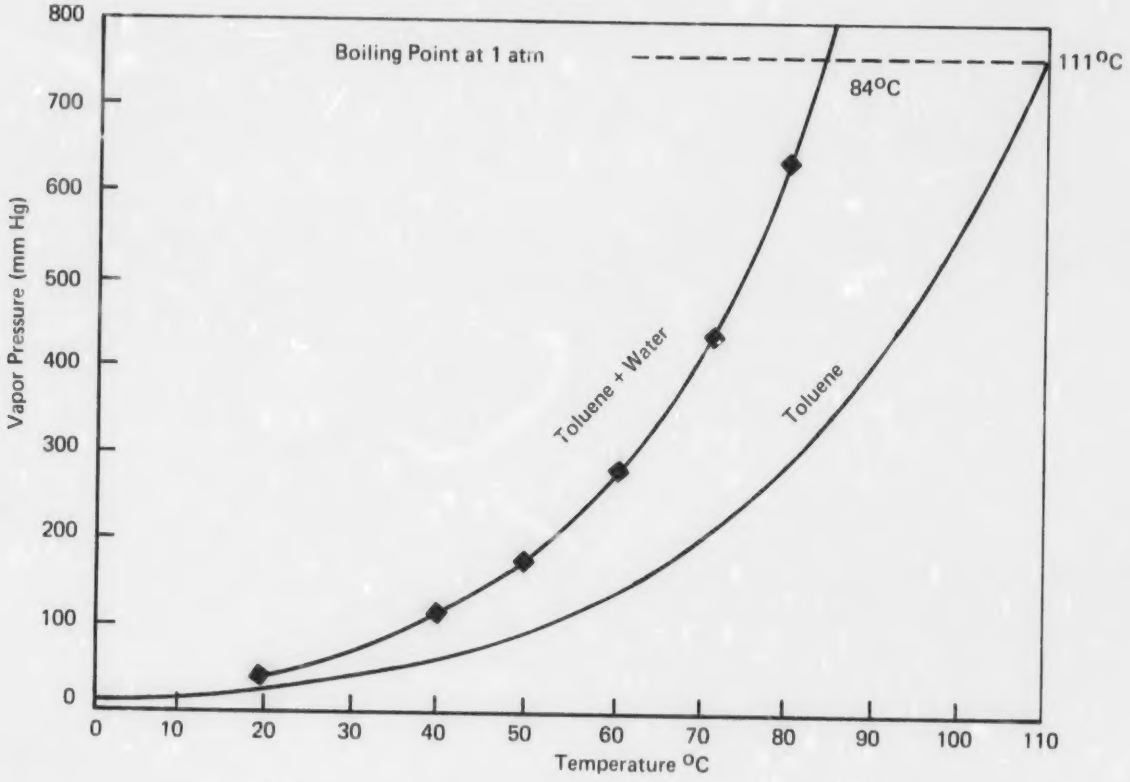

FIGURE 1 VAPOR PRESSURE OF TOLUENE, AND A TOLUENE/WATER MIXTURE

temperatures to be used in the distillation. This lowering of boiling point becomes very important in the case of heat sensitive materials or where there is a large amount of inert material present (i.e., steam distillation of turpentine from pine gum leaving rosin).

With a high concentration of non-volatile liquid present (as in the case of perchloroethylene recovery from waste degreasing solvent), the vapor pressure of the volatile component would decline as the concentration of volatile component was reduced, requiring progressively higher distillation temperatures, greater vacuum, or both. Steam distillation offers an important means of reducing the distillation temperature in this case as well.

1. Steam Distillation of Volatiles with Very Little Non-Volatile Liquid Present

In a batch steam distillation where the amount of non-volatile liquid is small in relation to the quantity of volatile component present, the weight of carrier steam required per lb of immiscible volatile can be calculated using the following equation (Ref. 1):

$$\frac{W_s}{W_{im}} = \frac{P_s M_s}{P_{im} M_{im}}$$

Where

W_s = weight of carrier steam required (lb)

W_{im} = weight of volatile, immiscible liquid distilled

P_s = partial pressure of steam (mm Hg)

P_{im} = partial pressure of pure volatile, immiscible, liquid (mm Hg)

M_s = molecular weight of steam (18)

M_{im} = molecular weight volatile immiscible liquid

and P_s and P_{im} are the vapor pressures of water and the pure component at the operating temperature.

Some additional steam or other source of heat is also required to heat the charge to the boiling point and supply the heat for vaporization of the volatile (water immiscible) component.

This simpler form of steam distillation has been applied to removal of residual volatiles from solvent extracted waste paper and wood chips that have been extracted for rosin and turpentine. In these examples, the volatile material is steam distilled from solid materials which did not influence the equilibrium vapor pressure of the volatile component.

2. Steam Distillation of Volatiles with Significant Non-Volatile Liquid Present

As the volatile component is steam distilled from the mixture, the vapor pressure of the volatile component decreases due to its solubility in the non-volatile component and the volume of carrier steam required per lb of volatile component distilled increases. In recovery of perchloroethylene from degreasing waste, for example, the concentration of perchloroethylene must be reduced to less than 100 ppm in the residual waste oil to allow the latter to be sold as boiler fuel. If steam distillation were not used, either high temperatures or high vacuum would be necessary to adequately reduce the residual concentration of perchloroethylene.

The quantity of steam required for steam distillation of a volatile component from a liquid mixture containing a high proportion of non-volatile liquid may be calculated using the following equation (Ref. 2):

$$W_s = 18 \left[\left(\frac{\pi}{EP_{im}} - 1 \right) \left(B_1 - B_2 \right) + \frac{\pi O}{EP_{im}} \ln \frac{B_1}{B_2} \right]$$

Where:

π = Total pressure in distillation system

B_1 = Initial quantity of volatile component in mixture (moles)

B_2 = Final quantity of volatile component in mixture (moles)

O = Quantity of non-volatile component in mixture (moles)

E = Vaporization efficiency – this factor will usually range from 0.9 for volatile components of molecular weight of less than 100 down to about 0.5 for compounds with a mol. wt of over 250 (lubricating oils).

3. Effect of Liquid Water in the Still

When there is liquid water in the still and the pressure is reduced, the temperature of the distillation is reduced. In this case, the ratio of carrier steam to volatile component distilled will remain nearly the same. By eliminating the presence of liquid water in the still, it is possible to decrease carrier steam requirements by decreasing the operating pressure of the still while holding the distillation temperature constant.

Steam distillation without a liquid water phase present can be accomplished by operating the still at a total pressure less than the sum of the vapor pressure of water and the volatile component at the operating temperature. This relationship between carrier steam requirements and operating pressure (at the operating temperature) is shown below (Ref. 3):

$$\frac{W_s}{W_{im}} = \frac{(\pi - P_{im}) M_s}{P_{im} M_{im}}$$

Where:

W_s = weight of carrier steam

W_{im} = weight of volatile, immiscible liquid distilled

P_{im} = vapor pressure of pure immiscible liquid at operating temperature

π = total pressure in the still

M_s = molecular weight of steam (18)

M_{im} = molecular weight of water immiscible volatile component

C. OPERATING CHARACTERISTICS

Steam distillation may be used for the recovery or purification of volatile organic materials (molecular weight up to about 300) from liquid wastes, inert solids, or in some cases, slurries. The organic material to be removed from the process or waste stream must have high enough a vapor pressure to co-distill with steam at a temperature low enough to prevent decomposition.

Continuous steam distillation is used in the petroleum industry for the production of gasoline and other petroleum products that utilize high boiling feedstocks. Continuous steam distillation is also used in the fractionation of crude tall oil into rosin and fatty acids.

When steam distillation is used to reduce the concentration of a volatile component to very low levels as in the case of turpentine production or waste treatment, it is normally conducted as a batch or semi-batch operation. In the case of a batch steam distillation, the still is charged, the charge heated to temperature and the distillation conducted by bubbling steam through the liquid phase. In semi-batch operation, the charge containing a high ratio of volatiles to non-volatiles is fed to the still continuously for a given period of time while the volatile component is steam distilled from the mixture. After the last of the feed is introduced, the steam distillation is continued until the volatiles are reduced to the desired residual concentration.

In addition to liquids, slurries, emulsions, sludges, and bulk solids may also be treated by steam distillation to remove volatile organics. This unit operation may be conducted in the presence of heavy metals, provided there is no chemical reaction.

Reactivity of the process or waste stream with water or steam is a limitation of this process. It is not possible to recover some chlorinated hydrocarbons from organic waste streams, for example, since the water (or steam) removes the stabilizer normally used in the chlorinated hydrocarbon and peroxide formation and/or decomposition takes place (Refs. 4,5). Nevertheless, some stabilizer systems are so designed that as the chlorinated solvent is steam distilled, the stabilizers are also steam distilled and are retained in the chlorinated solvent (for example, n-methyl pyrrole in Cl_3CO_3).

This process initially generates two output streams, the stripped waste (generally containing 100 ppm or less residual volatile component) and a vapor stream of volatile component and water vapor. The ratio of steam (or water) to volatile organic compounds in this vapor stream can be determined by the appropriate equations cited earlier in the text. This second stream is usually condensed, and in the case of a water-immiscible organic, the immiscible liquids are separated by gravity to generate a second and third stream; a liquid stream of nearly pure volatile component and a wastewater stream containing traces of the immiscible volatile component. In case of a water-soluble organic such as glycerine, the organic material may be recovered in a concentrated form by partially condensing the vapors and then the pure product recovered by evaporation, distillation, or other means.

D. EQUIPMENT AND MATERIALS

The equipment used for steam distillation in waste treatment is usually a batch distillation system with provision for bubbling steam through the charge in the batch still. In the petroleum industry, however, there is extensive use of continuous steam distillation in the production of gasoline, lube oils, naphtha, and fuel oil (Ref. 6). The still may be heated by heating coils in the still, a steam jacket around the still, or the live steam being bubbled through the charge in the still. The heat supplied in this manner is in addition to the live steam used as carrier steam and is required to raise the charge to the distillation temperature, supply heat for vaporization of the volatile organic and make up for any heat losses.

Feed pumps and tanks are also required as well as a condenser, gravity settling tanks, and product receiver tanks. A typical arrangement for a steam distillation system is shown in Figure 2.

For steam distillation of residual solvent from non-volatile solid materials (such as botanical material or wood fiber) a stationary or rotating vessel is used in place of the batch still with the necessary heat of vaporization being supplied by superheated carrier steam.

When sludges or liquids containing materials that may polymerize or precipitate out are treated by steam distillation, the batch still should be designed with removable tube heating bundles and adequate access to the still (through manholes or ports) to facilitate removal of solid deposits.

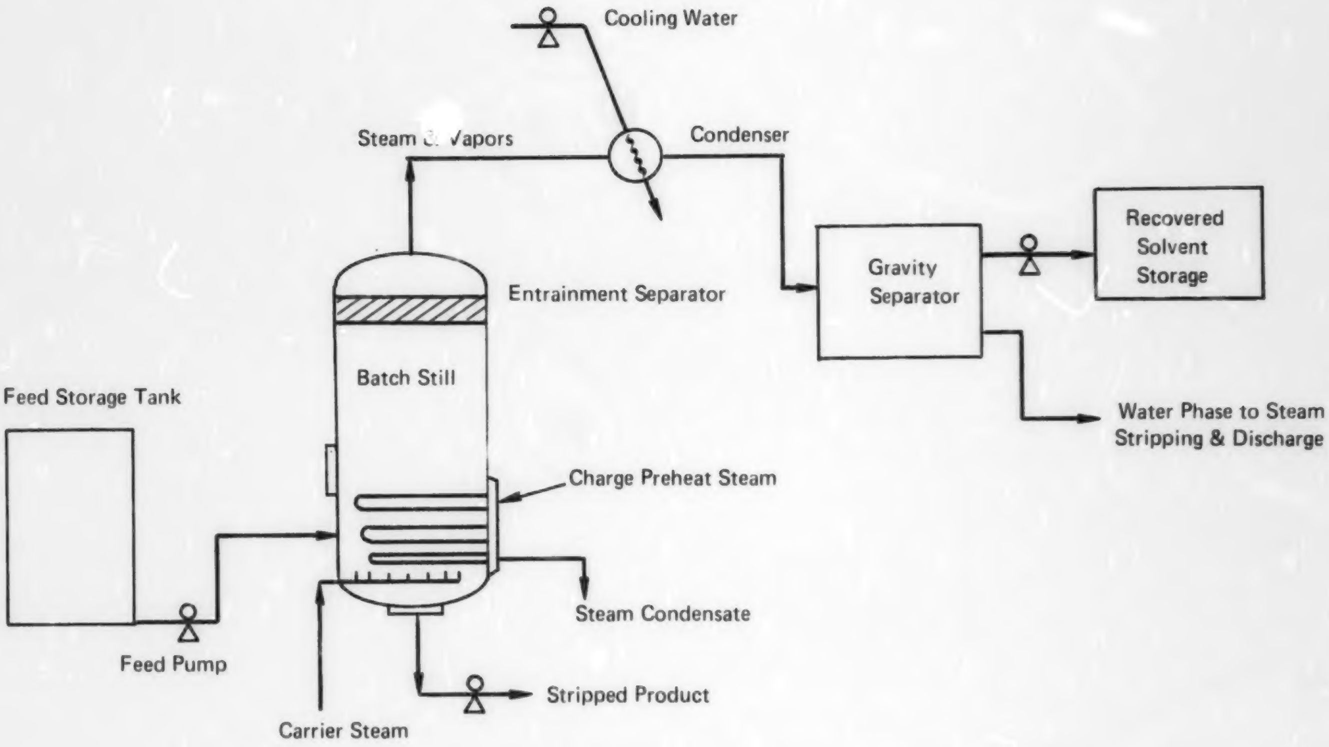
Cooling Water
Steam & Vapors
Condenser
Recovered Solvent Storage
Gravity Separator
Entrainment Separator
Batch Still
Feed Storage Tank
Water Phase to Steam Stripping & Discharge
Charge Preheat Steam
Steam Condensate
Feed Pump
Stripped Product
Carrier Steam

FIGURE 2 FLOW DIAGRAM FOR A TYPICAL STEAM DISTILLATION SYSTEM

III. APPLICATIONS TO DATE

A. INDUSTRIAL PRODUCTION

1. Petroleum Industry

Perhaps the widest application of this unit operation has been in the petroleum industry. Steam and feedstock are introduced into a conventional multi-tray distillation column to produce gasoline, lube oil, or naphtha. Without the use of steam, or steam and vacuum together, the high distillation temperature would result in vigorous decomposition. Steam distillation in this application is usually conducted on as a continuous operation. Steam distillation is also used in this industry for removing low boiling components from a mixture of components. This latter application of steam distillation in the industry is called "steam stripping" (Ref. 6). In these applications, it is not necessary for the volatile component to be removed completely so the efficiency obtained in these applications is determined by economic and product quality requirements.

2. Soap Industry

Glycerine is recovered from spent soap lye as a solution containing about 10% glycerine and 20% salt. This solution is concentrated, most of the salt crystallized out, and then the 80% crude glycerine is steam distilled. Because of the high boiling point of glycerine at atmospheric pressure and the possibility of decomposition at this temperature, vacuum is used to lower the distillation temperature. The steam in this case is used primarily as a carrier for the glycerine, since glycerine is water soluble. Considerable steam is required for this distillation and this would lead to a very dilute product if all the vapor were condensed in one stage. Therefore, a series of condensers is used, and nearly pure glycerine recovered from the first condenser which is run hot enough to prevent condensation of water, but cool enough to condense the glycerine. The more dilute glycerine recovered in the final condensers is recycled to evaporators for re-concentration, thus assuring almost complete recovery of glycerine.

3. Naval Stores Industry

In the Olustee process, oleoresin (pine gum) containing turpentine and rosin is dissolved in turpentine, filtered, and then steam distilled to produce turpentine and gum rosin. The turpentine vapor and steam are condensed and the two liquids separated by gravity. The molten rosin is drained from the kettle and cast into blocks.

4. Forest Products Industry

Fatty acids (and tall oil rosin) are obtained from crude tall oil, a by-product in the production of sulfate (kraft) wood pulp. The tall oil is fractionated by steam distillation under vacuum to yield various fractions of fatty acids and tall oil resin. The steam serves the dual functions of reducing the distillation temperature and excluding air which would degrade the fatty acids. By using one distillation column for separating the fatty acids from the rosin and a second column to fractionate the fatty acids, it is possible to conduct this process as a continuous operation.

5. Waste Paper Industry

Many waste papers contain contaminants such as wet strength resins, plastic coatings, and waxes that must be removed for reprocessing the wood fiber for reuse. A solvent extraction process called the "Polysolv" process has been developed for removing these water insoluble organics. After these organics have been extracted from the waste paper, residual solvent must be removed from the paper fiber before further processing. Steam distillation of the solvent-wet fiber results in nearly complete recovery of the solvent which is then recycled.

6. Coal Chemicals Industry

In the production of coke from coal there are quantities of aromatic hydrocarbons such as benzene, toluene, and xylene also produced. The vapors from the coke ovens are scrubbed with wash oil and then the wash oil is steam stripped to recover the aromatic hydrocarbons. Typically, the aromatic hydrocarbon content will be reduced from about 10% to about 0.5% in this steam stripping.

B. WASTE TREATMENT

Steam distillation is used in waste treatment as well as in production. It is used in waste treatment to remove volatile organic material from liquids, solids, slurries, or sludges. The volatile organic component is recovered for its value and its residual concentration is reduced sufficiently to allow the resulting liquid, solid, or sludge to be safely disposed of. Frequently, steam distillation is used for recovering a mixture of volatile hydrocarbons from a waste stream and the mixture of hydrocarbons then further separated by conventional distillation.

1. Pharmaceutical Industry Waste

Plant (botanical) material or animal glands from solvent extraction processes are "steam stripped" to steam distill and recover residual solvent while reducing the solvent level enough to allow the extracted material to be landfilled or marketed.

2. Contract Disposal

Numerous industrial wastes are treated by contract disposal companies using steam distillation to recover halogenated and non-halogenated hydrocarbons. In the case of the halogenated hydrocarbon wastes, some of these contain enough valuable halogenated hydrocarbon that the waste contractor will actually purchase the waste (Ref. 7).

Some examples of wastes treated by one waste disposal contractor using steam distillation include:

a. Degreasing Solvent Waste

Waste degreasing solvent containing between 30-50% chlorinated hydrocarbon (such as perchloroethylene) is steam distilled under vacuum to recover the chlorinated hydrocarbon (for resale) and reduce its concentration in the residual oil to less than 100 ppm. The residual oil can then be sold as boiler fuel.

b. Printing Ink Waste

Oil base printing inks that have been cleaned from the presses and feedtanks using solvent generate a flammable waste containing the ink residue and naphtha. This solvent is recovered from the printing ink waste by steam distillation using a batch distillation system incorporating a removal tube heating bundle. The solvent concentration in the steamed waste must be reduced in this case to a level low enough (200-500 ppm) to preclude any fire hazard and the residue is then landfilled.

c. Paint Waste

Paint waste generated from cleaning tanks contains pigments, oils, binders, and the solvent used for cleaning these tanks. The solvent is recovered by steam distillation for resale and reuse. As in the case above, the still must be constructed to allow easy removal of the heating surface and access for cleaning out residue deposited in the still.

d. Shoe Manufacturing Waste

From a contaminated solvent mixture of chlorinated benzenes, the mono and dichlorobenzene are recovered by steam distillation but the trichlorobenzene in the waste has too high a boiling point to be economically recovered by steam distillation. Presumably, the concentrated waste containing the trichlorobenzene is disposed of by incineration after removal of the mono and dichlorobenzene.

e. Electronics Industry Polymer Masking

A polymer is used to protect portions of circuit boards that are being etched. This polymer mask is later removed by using a chlorinated hydrocarbon solvent to generate a chlorinated hydrocarbon waste containing about 10% polymer. The chlorinated hydrocarbon is recovered by steam distillation. At a concentration of about 50% polymer, the polymer begins to precipitate out of solution, thus necessitating that the still be constructed (as in the case of the ink and paint wastes) to allow ready access for cleaning.

f. Halogenated Hydrocarbon Wastes

As indicated earlier in the text, many halogenated hydrocarbons can be readily recovered from waste streams by steam distillation, but some caution must be exercised in insuring that all the stabilizer has not been removed from the halogenated hydrocarbon and that there has not been peroxide formation (Ref. 5). In some cases, additional stabilizer will be added prior to steam distillation, while in other cases this can be taken care of by the use of suitable stabilizers that will remain with the chlorinated hydrocarbon.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

The major energy requirement for this process is the steam used as carrier for co-distilling the volatile organic component(s) from the process or waste stream. In addition, steam (or heat supplied by other means) is required to raise the process or waste stream to the distillation temperature and supply the heat of vaporization of the volatile organic component.

A small amount of electrical energy is also required for the pumps that feed the distillation unit and supply cooling water.

The following is a sample calculation of energy requirements for the recovery of perchloroethylene from degreasing solvent waste:

Basis:

Feed		3,000 gal of solvent degreasing waste containing 13,500 lb of perchloroethylene (MWt 166) 13,500 lb of grease and oil (MWt 250)
Products	1	13,500 lb (2,000 gal) of grease and oil containing 1 lb of perchloroethylene
	2	13,500 lb (1,000 gal) of trichloroethylene
	3	4,000 gal wastewater containing a trace of perchloroethylene

The perchloroethylene can be separated from the oil by steam distillation because: (1) the perchloroethylene is chemically stable in the presence of water (steam) at the distillation temperature and (2) the vapor pressure of the oil/grease mixture at the distillation temperature is negligible.

At atmospheric pressure the initial temperature of distillation will be about 84°C. The temperature will gradually approach 100°C as the concentration of the perchloroethylene in the oil/grease mixture approaches 100 ppm.

The total carrier steam requirement can be calculated using the following equation for distillation of volatiles with significant non-volatile liquid present.

$$W_s = 18\left[\left(\frac{\pi}{EP_{im}} - 1\right)\left(B_1 - B_2\right) + \frac{\pi O}{EP_{im}} \ln \frac{B_1}{B_2}\right]$$

Where

B_1 = 13,500 lb/MWt 166 = 81.325 moles perchloroethylene

B_2 = 1 lb/MWt 166 = 0.006 moles perchloroethylene

π = 760 mm Hg

E = 0.7

P_{im} = 438.5 mm Hg (at 100°C)

O = 13,500 lb/MWt 250 = 54.0 moles

$$W_s = 18\left[\left(\frac{760}{0.7 \times 438.5} - 1\right)\left(81.325 - .006\right) + \frac{(760)(54)}{0.7 \times 438.5} \ln \frac{81.325}{.006}\right]$$

$$W_s = 18\,[(1.476)(81.319) + 1271] = 18\,(1391) = 25{,}000 \text{ lb carrier steam}$$

It is interesting to note that if it were not for the presence of the non-volatile components (oil and grease) the quantity of carrier steam required for the steam distillation would only amount to:

$$W_s = \frac{P_s\,M_s}{P_{im}\,M_{im}} \times W_{im} = \frac{(760)\,(18)}{(438.5)\,(166)} \times 13{,}500 = 2540 \text{ lb carrier steam}$$

In addition to the carrier steam, heat (steam) is required for (1) the heat of vaporization of the perchloroethylene, (2) raising the temperature of the charge to 100°C and (3) heat losses.

(1) heat of vaporization (50 cal/gm) 90 Btu/lb x 13,500 lb = 1,215,000 Btu
of perchloroethylene = 1,300 lb steam at 120°C

(2) heating charge from 60°F to 212°F
oil and grease 13,500 lb x (212-60)°F x 0.70 Btu/lb°F = 1,436,400 Btu
perchloroethylene 13,500 lb x (212-60)°F x 0.37 Btu/lb°F = 759,200 Btu
2,195,600 Btu =
2,300 lb
steam at 120°C

(3) heat losses at 2% total heat input

total input before losses 25,000 lb + 1,300 lb + 2,300 lb = 28,600 lb
(carrier) (vaporization) (preheat)

heat losses = 28,600 x 0.02 = 600 lb

Total Steam Requirement = 29,200 lb

Power Requirements

$$2 \text{ pumps} \times \tfrac{1}{2}\text{ HP} \times \frac{1\text{kWh}}{\text{HpHr}} \times 2\text{ hr/day} \times 3\text{ days} = 6\text{ kWh}$$

$$2 \text{ pumps} \times \tfrac{1}{2}\text{ HP} \times \frac{1\text{kWh}}{\text{HpHr}} \times 8\text{ hr/day} \times 3\text{ days} = \underline{24\text{ kWh}}$$

30 kWh/3,000 gal feed

Summary of Energy Requirements from Sample Calculation

Steam	29,200 lb of steam per 3,000 gal of treated degreasing waste or 1,000 gal of recovered perchloroethylene
Power	30 kWh per 3,000 gal of treated degreasing waste or 1,000 gal of recovered perchloroethylene

B. ENVIRONMENTAL IMPACTS

Aside from the environmental impact of generating the steam and power required for operating this process, the environmental impacts are those associated with disposal of the treated waste after the volatile component has been removed (to a residual level of 50-100 ppm volatile component) and the wastewater from the condensed steam. The wastewater will contain trace amounts of the volatile organic and may have to be treated (i.e., steam stripped) prior to disposal.

C. ECONOMIC ANALYSIS

The equipment shown in Figure 2 would be required for the example cited in Section IV-A. Cost estimates are given in Table 1. Estimated operating costs for perchloroethylene recovery by steam distillation are given in Table 2.

This treatment cost cited in this example is based on new equipment. Typically, contract waste disposal/recovery companies will purchase second-hand equipment when possible. This could reduce the fixed costs to about $200 per gallon and the treatment cost to about $0.53 per gallon of treated waste in this example.

Credits for the perchloroethylene at $2 per gallon and $0.05 per gallon for the oil/grease mixture (sold as boiler fuel) would more than offset the treatment cost for this degreasing waste.

TABLE 1

CAPITAL INVESTMENT STEAM DISTILLATION UNIT FOR 750 GAL/DAY SOLVENT WASTE

		Purchased Equipment (Jan. 1976)
Feed Storage	3,000 gal carbon steel	$ 5,000
Batch Still	1,000 gal carbon steel	16,000
Condenser	100 sq ft 304 Stainless	4,500
Gravity Separator	1,000 gal carbon steel	1,800
Product Storage	2,000 gal carbon steel	3,300
Four Pumps 304 Stainless with Explosion Proof Motors		6,300
		$ 36,900
Total Capital Investment*		$129,150
Round to		$130,000

*Includes piping, wiring, insulation and instrumentation.
Excludes steam boiler; boiler capital and operating charges are included in the cost of steam.

Source: Arthur D. Little, Inc., estimates.

TABLE 2

ESTIMATED OPERATING COSTS FOR PERCHLOROETHYLENE RECOVERY BY STEAM DISTILLATION

Waste Stream: 3,000 gal per week of degreasing waste solvent containing 13,500 lb (1,000 gal) perchloroethylene + 13,500 lb (2,000 gal) of oil and grease

Operation: 240 days per year, one shift per day

Capital Investment: $130,000

Variable Costs	**$/Unit**	**Units/3000 Gal Treated Waste**	**$/3000 Gal Treated Waste**	**Annual Cost***
Setup & Operating Labor (Includes Supervision plus Overhead)	12.00/man hr	60	$ 720	--
Analytical Support	15.00/man hr	20	300	--
Steam	4.00/1000 lb	29.2	117	--
Cooling Water	0.08/1000 gal	150	12	--
Electric Energy	0.02/kWh	30	1	--
Wastewater Treatment	1.00/1000 gal	4	4	--
Maintenance	5 days/240 days		270	13,000
Variable Cost – sub-total			$1,424	
Fixed Costs				
Capital Recovery (10 years @ 10%)	$\frac{5\text{ days}}{240\text{ days}}$		432	20,800
Taxes and Insurance (@ 2% Cap. Inv.)	$\frac{5\text{ days}}{240\text{ days}}$		54	2,600
Fixed Cost – sub-total			$ 486	
Total Treatment Cost			$1,910 per 3000 gal treated waste ($0.64 per gal treated waste)	

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*On an annualized basis – this steam distillation unit would not be used year-round on this one waste stream, but would be used for treating a variety of waste streams.

Source: Arthur D. Little, Inc., estimates.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Steam distillation offers an effective means of removing volatile hydrocarbons from liquids, slurries, sludges, or solids.

It is widely used as an industrial production process and is also used extensively in waste treatment. As a waste treatment process, it is capable of reducing residual volatile organics in a waste to levels of 100 ppm or less.

Its prime limitations are related to the volatility of the component(s) being removed by steam distillation and any reactivity of the waste with steam or water. The waste must also be in a form that can be effectively contacted with water or steam.

With the increase in cost (value) of hydrocarbon solvents (particularly the chlorinated hydrocarbons) and the increasingly stricter regulations regarding the landfilling of sludges containing hydrocarbon solvents, the use of steam stripping for recovery of marketable volatile hydrocarbons will become more widespread. Without marketable by-products, any growth in the use of steam distillation for waste treatment will depend on regulations governing landfilling of sludges.

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4. Private Communication, J. Miserlis of Silresim, Inc., Lowell, Mass.

5. Kirk-Othmer, *Encyclopedia of Chemical Technology*, 2nd ed, John Wiley & Sons, N.Y., 1964, Vol. 5, pp. 148-203.

6. Nelson, Wilbur L., *Petroleum Refining Engineering*, McGraw-Hill, N.Y., 1958.

7. Private Communication, J. Miserlis, Silresim, Inc., Lowell, Mass.

B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD

Commercial contract waste disposal companies that practice steam distillation as a method of waste treatment include:

Silresim, Inc.
86 Tanner Rd.
Lowell, Mass.

Industrial Tank, Inc.
P.O. Box 831
310 Berrelesa St.
Martinez, Cal. 94553

Seymour Mfg. Co.
500 B. Broadway
Seymour, Indiana 47274

In addition to these contract waste disposal companies, steam distillation is used for product recovery in the following industries:

Petroleum – Used in refining various hydrocarbon feedstocks and used for raising flash points of some products by reducing volatiles.

Naval Stores – Turpentine is steam distilled from pine gum.

Coal Chemicals – Aromatics are recovered from coke oven gas.

Soap Production – Glycerine is recovered as a by-product of soap production.

Waste Paper – residual solvent is recovered from waste paper fiber.

AIR STRIPPING

Prepared by

Lawrence R. Woodland

I. CONCLUSIONS AND RECOMMENDATIONS

Air stripping has one major industrial application–The stripping of ammonia from domestic wastewater. The application of air stripping to the removal of other gases or volatile components from dilute aqueous streams would depend on the environmental impact of the air emissions that resulted. If sufficiently low concentrations are involved, the gaseous compounds can be emitted directly to the air. Otherwise, air pollution control devices may be needed–making the economics less favorable.

II. PROCESS DESCRIPTION

A. BACKGROUND

Air stripping of ammonia from biologically treated domestic wastewater is being developed as a means of reducing nitrogen content in wastewater. Ammonia removal efficiencies of over 90% have been obtained in pilot scale tests using packed towers and a wastewater containing 60 ppm (ammonia) nitrogen. Air stripping systems other than packed towers (such as holding ponds, holding ponds with surface agitation and spray ponds) have been investigated as means of stripping ammonia from wastewater, but the packed tower appears to be the most compact and efficient (Ref. 1).

Ammonia removal efficiencies in a full-scale, 15 mgd, air stripping tower at the Orange County, California Water District Plant have averaged only 60-65%, but they expect to increase this to up to 95% when tower modifications are completed this year (Ref. 2).

Air stripping of the wastewater, removes the ammonia nitrogen from the wastewater and discharges it to the air. The concentration of ammonia in the air leaving the South Tahoe, California, stripping tower is about 6 mg/m³, well below the odor threshold of 35 mg/m³ and well below existing standards of 100-200 mg/m³ (Czechoslovakia and U.S.S.R.) The U.S. has no standards for ammonia (Ref. 3).

Air stripping of ammonia from wastewater is limited to dilute ammoniacal solutions, since the emission level of ammonia would be too high from a concentrated solution. In addition, ammonia would be more efficiently recovered from concentrated solution by steam stripping.

B. UNDERLYING PRINCIPLES

Ammonia is quite soluble in water, but this solubility is temperature dependent. Data from the "Handbook of Chemistry and Physics" (Ref. 4) on the solubility of ammonia in water at different temperatures are presented below:

Temp.	$gmNH_3$/gm water (at 1000 mmHg)
0°C	1.094
20°C	0.629
40°C	0.386

The relationship between temperature and the solubility of ammonia for dilute ammonia solutions is expressed by Henry's Law:

$$y = Mx$$

where:

y = mole fraction NH_3 in the vapor
x = mole fraction NH_3 in the liquid
M = Henry's constant

Henry's constant (M) is a function of temperature as shown in Figure 1. By raising the temperature of the wastewater the vapor pressure of the ammonia is increased and ammonia removal efficiency increased.

Another factor in ammonia removal efficiency is the pH of the wastewater. A portion of the ammonia dissolved in the water reacts with the water to give the following equilibrium:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

By increasing the pH (concentration of OH^-) the equilibrium is shifted to the left, reducing the concentration of NH_4^+ and increasing the concentration of free dissolved ammonia.

C. OPERATING CHARACTERISTICS

To obtain reasonable ammonia removal efficiencies (or rates) by air stripping, either the temperature or the pH of the wastewater must be increased. In steam stripping ammonia from "sour water" the temperature of the wastewater is increased from about 38°C to about 110°C. The pH of the "sour water" ranges from 8-9 (unless it is not acidified to aid release of the H_2S).

In air stripping of ammonia from dilute wastewater, the air temperature limits the effectiveness of heating the wastewater. Ammonia removal efficiency is enhanced instead by increasing the pH.

1. Process Feed

Removal of ammonia from biologically treated domestic wastewater by air stripping as part of a tertiary treatment system offers a unique economic opportunity. This is because part of the tertiary treatment scheme involves lime addition for phosphate removal. This lime addition significantly increases the pH. The wastewater can then be air stripped at this high pH.

Figure 2 is the flow diagram for the air/ammonia stripping system as applied to the treatment of domestic wastewater at the Orange County, California Water District. This same system could be used for treating other aqueous ammonia or volatile organic containing wastes, but would be subject to air emission regulations and the fact that the ammonia or organic in the dilute air stream leaving the towers could not be economically incinerated or recovered.

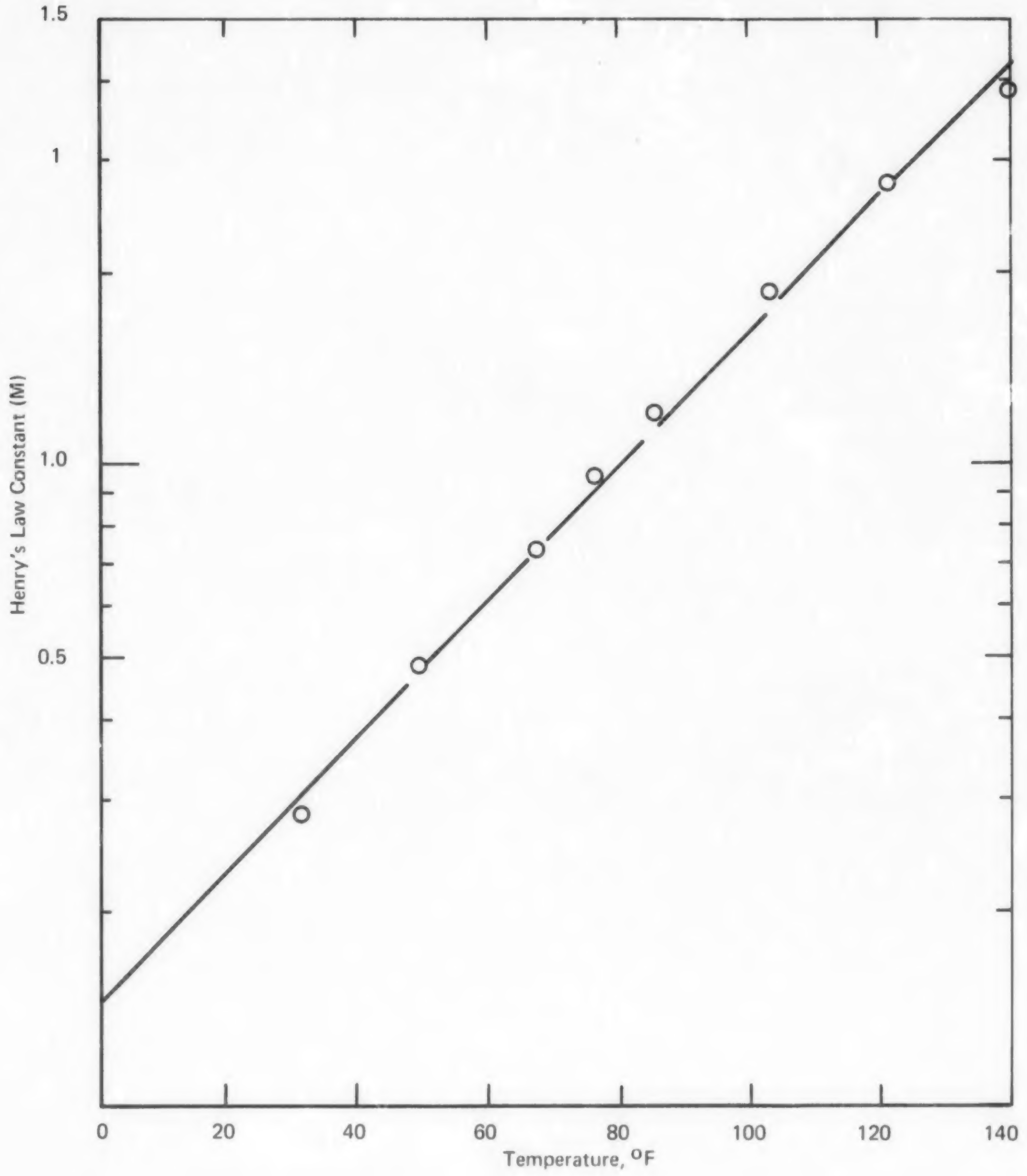

FIGURE 1 HENRY'S LAW CONSTANT AS A FUNCTION OF TEMPERATURE

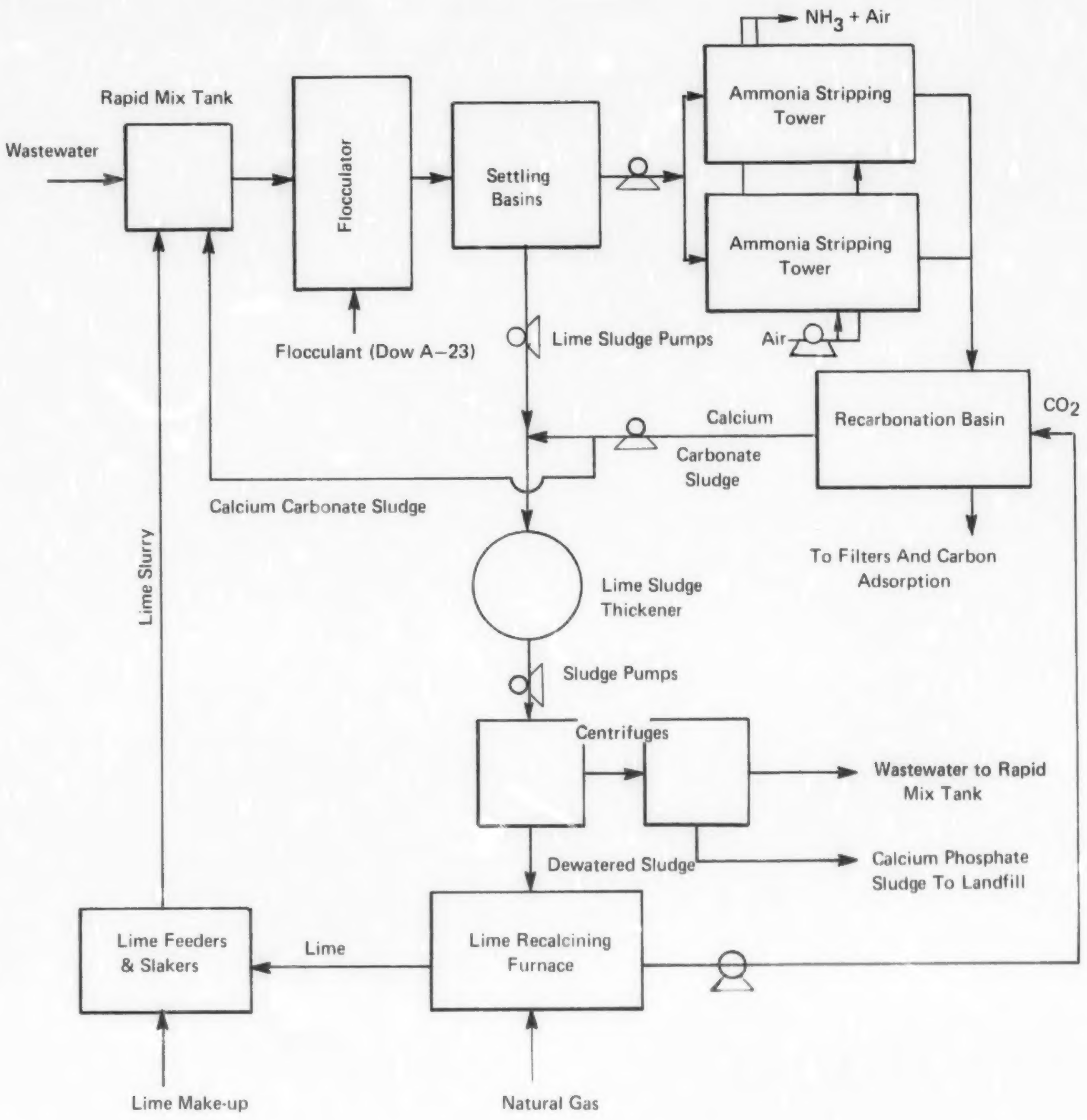
NH$_3$ + Air
Rapid Mix Tank
Wastewater
Flocculator
Settling Basins
Ammonia Stripping Tower
Ammonia Stripping Tower
Lime Sludge Pumps
Air
Flocculant (Dow A–23)
Calcium Carbonate Sludge
Recarbonation Basin
CO$_2$
Calcium Carbonate Sludge
To Filters And Carbon Adsorption
Lime Slurry
Lime Sludge Thickener
Sludge Pumps
Centrifuges
Wastewater to Rapid Mix Tank
Dewatered Sludge
Calcium Phosphate Sludge To Landfill
Lime Feeders & Slakers
Lime
Lime Recalcining Furnace
Lime Make-up
Natural Gas

FIGURE 2 AIR STRIPPING OF AMMONIA FROM BIOLOGICALLY TREATED DOMESTIC WASTEWATER

D. PROCESS OPERATION AND EQUIPMENT

The ammonia containing wastewater and the lime slurry are fed to a rapid mix tank. Following the rapid mix tank are flocculators and a settling basin, where calcium phosphate precipitates and recirculated calcium carbonate settle out. The clarified, lime-treated, wastewater is pumped to the top of two packed towers. In each of the towers, six fans developing 350,000 cfm each draw air up through the tower countercurrent to the failing wastewater. The "packing" in the tower is actually a series of bundles of 1/2 inch PVC pipe with the pipe sections spaced 2-3 inches on center. The pipe sections are horizontal and the direction of each row alternates. The design criteria for this unit are as follows:

Hydraulic loading:	1 gpm/sq ft
Air Flow:	400 cu ft/gal
Depth of "Packing":	25 ft
Temperature of Operation:	16-40°C

As discussed earlier, the ammonia removal efficiency in this unit varied with temperature averaging 65% for April-June 1975 and 60% for Sept.-Dec. 1975. This efficiency is expected to be increase to up to 95% when modifications to the tower now underway are complete. The towers are being modified to prevent bypassing of the air flow around (rather than through) the tube bundles.

After the wastewater has been air stripped of ammonia, it flows into the recarbonation basin where compressed carbon dioxide rich gas from the lime recalcining furnace is bubbled through it to precipitate calcium carbonate. Some of the calcium carbonate sludge is returned to the rapid mix tank to enhance flocculation while the remainder of the calcium carbonate sludge and the phosphate sludge from the settling basins are sent to the centrifuges. Here the sludges are fractionally centrifuged to yield two dewatered sludges, one rich in calcium carbonate that is sent to the lime kiln and one containing phosphate that is sent to landfill.

The calcium carbonate is recalcined to supply regenerated lime to the system. About 24 tons lime per day are recycled to the process when the system is operated at a 15 mgd wastewater flow rate, 6 tons per day of makeup lime is required.

III. APPLICATIONS TO DATE

A. AMMONIA FROM DOMESTIC WASTEWATER

Various systems for air stripping of ammonia from wastewater have been proposed and investigated. These include: holding ponds, holding ponds with surface agitation, spray ponds, and packed towers.

The packed tower appears to be the most compact and efficient (Ref. 1). Full-scale packed towers have been used at South Tahoe, California and the Orange County, California Water District Plant. The full-scale unit at South Tahoe operated in the summer at efficiencies equivalent to those of the pilot stripper (over 95% removal of NH_3 at a pH of about 10.0), but in the winter when the air temperature dropped to -7°C ammonia removal dropped to 30% (Ref. 5). There was also a calcium carbonate scale buildup problem in this tower which required periodic acid cleaning of the tower.

The packed tower at the Orange County Water District Plant has a different type of packing (PVC pipe) that does not accumulate deposits. An important factor in preventing solids deposits is operation of the setting basins or clarifier prior to the stripping tower to preclude any carryover of suspended solids. Ammonia removal efficiencies over the first six months of operation of the Orange County have only ranged from 60% in the winter to 65% in the spring. When the modification of the towers (to prevent air bypassing the packing) is completed this year, ammonia removal efficiencies are expected to approach 95%. Since the climate is warmer in Orange County than at So. Tahoe, this stripper should not suffer the same cold weather loss of efficiency.

B. AMMONIA FROM PETROLEUM WASTEWATER

Prather has reported several studies in which ammonia was removed from petroleum refinery wastewater by stripping with air (Refs. 6-8). The concentrations of ammonia-nitrogen in the untreated wastewater averaged slightly more than 100 mg/l. When 300 cu ft of air were applied per gallon of wastewater, the ammonia removal was found to be 85% at a pH of 10.5 and 34% at a pH of 9.4. In another study, in which the wastewater was passed through a closely packed aeration tower with 480 cu ft of air supplied per gallon, ammonia-nitrogen removal by air stripping was found to be very effective (more than 95% removal) at any pH above 9.0. When the pH fell below 9.0, the ammonia-nitrogen removal decreased sharply. The removal fell to 91% at a pH of 8.9 and to 58% at a pH of 8.8.

At the low concentration of ammonia cited in these studies (~ 100 ppm), air stripping would indeed be a practical means for NH_3 removal. For the high concentrations of ammonia typically present in refinery "sour water" (2000-10,000 ppm) air stripping could result in serious air emission problems.

IV. ENERGY, ENVIRONMENTAL ISSUES, AND ECONOMICS

A. ENERGY REQUIREMENTS

As previously mentioned, there are two major means for improving ammonia removal from wastewater. One is to increase the wastewater temperature (requiring heat) and the other is to increase the pH of the wastewater (requiring alkali).

In air stripping of ammonia from dilute solution in wastewater, it would not be practical to heat the wastewater hot enough to remove the residual ammonia. If ambient air were used for stripping, the wastewater heat loss would be extremely high.

The other means of increasing the ammonia removal rate (and efficiency) is to increase the pH. This method is ideally suited to the removal of ammonia from tertiary treated domestic wastewater since the phosphate removal step in tertiary treatment requires a high pH. Lime slurry is added to the wastewater prior to air stripping and then is recovered using flue gas from the recalciner. The recalciner calcines the recovered lime sludge to generate reactivated lime and carbon dioxide for the recarbonators.

Although the lime addition also serves the function of phosphate removal, for purposes of arriving at energy requirements and operating cost, all of the energy required for lime treatment (and recovery) is included in our estimates.

The following is a summary of operating (electrical) power requirements for treating 15 million gallons per day (mgd) wastewater.

	HP		HP
Feed Pumps	110	CO_2 Compressors	160
Rapid Mix Tank	10	Sludge and Mud Pumps	30
Flocculator, Clarifier	35	Centrifuges	80
Cooling Tower Pumps	400	Rotary Hearth Recalciner	75
Cooling Tower Fans*	900	Lime Preparation	10

(*Can range from 660-1500 HP)

Total operating HP - 1810 or 1600 kwh/hr

Natural gas is required for the recalciner; this amounts to about 8 million Btu (8000 cu ft) natural gas per ton of feed or 192 million Btu/day.

B. ENVIRONMENT IMPACT

When the concentration of ammonia in the wastewater is about 23 ppm and the air to water ratio is 500 ft^3/gal, the concentration of ammonia in the saturated air leaving the tower is about 6 mg/m^3. This is well below the odor threshold concentration of 35 mg/m^3. There are no U.S. standards for ammonia emissions, but Czechoslovakia and the U.S.S.R. have established limitations of 100 and 200 mg/m^3, respectively (Ref. 3). In regard to ammonia washout by rainfall the following paragraph from Reference 3 indicates that potential rainfall washout to receiving streams does not pose a hazard.

"Calculations for the ammonia washout in a rainfall rate of 3 mm/hr (0.12 in./hr) have been made for the Orange County, California project. The ammonia concentrations of ammonia in the rainfall would approach natural background levels within 16,000 feet of the tower. Of course, the ammonia discharge during dry periods diffuses into the atmosphere quickly so that the background concentration and resulting washout rate of ammonia at greater distances from the tower are not affected during a subsequent storm. The ultimate fate of the ammonia that is washed out by rainfall within the 16,000-foot downwind distance depends on the nature of the surface upon which it falls. Most soils will retain the ammonia. That portion which lands on paved areas or directly on a stream surface will appear in the runoff from that area. Even though a portion of the ammonia washed out by precipitation will find its way into surface runoff, the net discharge of ammonia to the aquatic environment in the vicinity of the plant would be very substantially reduced."

The treated wastewater should be low enough in residual ammonia (< 5 ppm) to allow safe discharge to a receiving body of water.

About 25 tons per day of dewatered calcium phosphate, magnesium and calcium carbonate sludge must be disposed of by landfill for a 15 mgd plant. This sludge disposal will require a significant amount of land, but should not pose any environmental hazard.

C. ECONOMIC ANALYSIS

1. Capital Investment

The capital investment figures reported in 1973-1974 for the ammonia stripping section of Water Factory No. 21 are as shown in Table 1 (Ref. 9).

As indicated in Section IV-A, the cost of lime handling and recovery (sludge treatment and recarbonation) have been included in this report as part of the air stripping process.

The capital investment adjusted to January 1976 using the Chemical Engineering Plant Cost Index would be $7,800,000.

2. Operating Cost

The estimated operating cost for this unit operation is summarized below in Table 2.

TABLE 1

CAPITAL INVESTMENT FOR AIR STRIPPING OF AMMONIA FROM 15 MGD WASTEWATER

Section of Plant	**Capital Investment**
Influent Pipelines and Pump Station	$ 341,000
Clarification	756,000
Ammonia Stripping	2,834,000
Recarbonation	381,000
Sludge Treatment (Includes Recalcination)	1,688,000
Land	200,000
Engineering (at 10%)	620,000
	$6,820,000

Source: Arthur D. Little, Inc., estimates

TABLE 2

OPERATING COST FOR AIR STRIPPING OF AMMONIA FROM 15 MGD WASTEWATER

Fixed Capital Investment: $7,800,000

Waste Stream: 15 mgd (15 million gallons per day) biologically treated domestic wastewater containing 60-100 ppm NH_3

Outputs: 15 mgd treated wastewater containing $\sim$ 5 ppm NH_3
25 tons/day wet calcium phosphate waste sludge
5 tons ammonia/day to the atmosphere at 6 mg/m^3

Operation: 350 days/yr, 24 hr/day

	$/Unit	Units per 1000 gal Wastewater	Cost for 1000 gal Wastewater ($)	Annual Cost ($)
Variable Costs				
Operating Labor (2 men/shift)	12.00	–	.038	200,000
(Daily) Instrument Maint. (20 hrs/wk)	15.00	–	.003	16,000
Electrical Energy	0.02/kWh	.25600	.051	270,000
Natural Gas or Oil	2.00/MMBtu	.0128	.026	134,000
Sludge Disposal	10.00/ton	.0018	.018	96,000
Makeup Lime	35.00/ton	.0004	.014	74,000
Maintenance (@2% Inv/yr)		–	.029	150,000
Total Variable Costs			**0.179**	**$ 940,000**
Fixed Costs				
Capital Recovery (10 years at 10%)			0.242	1,270,000
Taxes & Insurance (@2% Inv.)			0.029	150,000
Total Fixed Costs			**0.271**	**1,420,000**
Total Treatment Cost			**$0.45**	**$2,360,000 per year**

Source: Arthur D. Little, Inc., estimates

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

The future application of air stripping of volatiles from wastewater will be limited to those volatiles that will not cause an air emission problem. Air stripping of ammonia from treated domestic wastewater dilute solutions of ammonia (with no other volatiles) is a good application. It is unlikely that many applications other than this one will be found for air stripping of wastewater.

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B. PEOPLE AND ORGANIZATION EXPERIENCED IN THIS FIELD

The prime industrial contact for information on this wastewater treatment method is:

Mr. William Blansett
Water Factory 21
Orange County Water District
10500 Ellis Ave.
Fountain Valley, Cal. 92703

STRIPPING, STEAM

Prepared by

Lawrence R. Woodland

I. CONCLUSIONS AND RECOMMENDATIONS

Steam stripping is a proven process which is generally used for removing volatile (organic chemical) compounds from aqueous process water or wastewater. Sufficient data exists for the design of steam strippers for many industrial production processes and wastewater treatment applications. For new applications involving multiple volatile components, laboratory or bench scale investigation would be necessary.

We recommend that steam stripping be considered whenever amenable components such as volatile organics, H_2S or NH_3 are present in the waste steam.

II. PROCESS DESCRIPTION

A. BACKGROUND

Steam stripping has been used for many years for the recovery of ammonia from coke oven gas. Indeed, this was at one time the only industrial source of ammonia. The flue gas from the coke oven gas is scrubbed with water and then the ammonia is recovered by adding lime to the scrubber water and steam stripping out the ammonia.

Sulfur is recovered from refinery "sour water" as H_2S by steam stripping the sour water. Along with the H_2S, ammonia and a small amount of phenol are also removed from the sour water in the steam stripping operation.

Recently, as water effluent regulations have become more stringent, other aqueous waste streams are being treated by this unit operation for removal of volatile organic components (i.e., methanol from pulp mill condensate).

B. UNDERLYING PRINCIPLES

Steam stripping is essentially a fractional distillation of volatile compounds from a wastewater stream. The volatile component may be a gas or volatile organic compound with solubility in the wastewater stream. In most instances, the volatile component, such as methanol or ammonia, is quite water soluble. More recently, this unit operation has been applied to the removal of water immiscible compounds (chlorinated hydrocarbons) in wastewater that must be reduced to trace levels because of their toxicity.

1. Data Required for Process Design

Steam strippers may be designed for pure non-reactive volatile components in the wastewater by using tray-by-tray calculations and vapor/liquid equilibrium data reported in the literature. Unfortunately, a "wastewater stream" rarely contains only non-reactive components. If the volatile components react with each other, as in the case of refinery sour water containing H_2S and ammonia, the vapor pressure exerted by each of these components in water solution no longer follows Raoult's Law. An excellent treatise on the effect of interaction between these two water soluble gases on their vapor pressure is presented in a book by Beychok (Ref. 1). In this same reference, Beychok gives examples for the design of "sour water" strippers and some performance data for commercially operating units. Empirical relationships for sizing packed tower steam strippers for treating refinery sour water have also been developed (Ref. 2).

Where vapor/liquid equilibrium data does not exist for a specific combination of water soluble components, this data must be developed experimentally.

The Robert S. Kerr Environmental Research Laboratory of the EPA located in Ada, Oklahoma, is currently sponsoring a research program studying removal of water immiscible organic compounds (chlorinated hydrocarbons) from wastewater by steam stripping. The vapor/liquid equilibrium data generated in this program should prove useful in predicting steam stripping efficiencies for water immiscible compounds in wastewater (Ref. 3). Removal efficiencies of light chlorinated hydrocarbons of up to 90% have been obtained in 3-foot diameter x 20-foot high packed columns with feed streams containing 3,000-6,000 ppm chlorinated hydrocarbon.

2. Steam Stripper Efficiency

Steam stripper efficiency is not only a function of the number of vapor/liquid contact stages and steam input, but also temperature and pH. Temperature affects the solubility of gases in water. The vapor pressure of gases that dissolve in water to form acids or bases in solution are influenced by the pH of the wastewater. Beychok in his book describes how the mole ratio of NH_3 to H_2S and pH effect the partial pressures of these two gases over aqueous solutions (Ref. 1). By lowering the pH, more dissolved ammonia (as ammonium ion) is "tied up" as the ammonium salt of the added acid, thus liberating the H_2S. Removal efficiency of H_2S is therefore increased by adding acid. Likewise, ammonia removal efficiency is increased by adding caustic to the wastewater.

At one time, the only objective in stripping sour water was to remove hydrogen sulfide (H_2S), but more stringent effluent water quality regulations now require efficient removal of ammonia. Shell (Ref. 4) and Chevron (Ref. 5), and perhaps other refiners, steam strip sour water in two stages (at different pH's) in order to maximize both hydrogen sulfide and ammonia removal.

Other factors that effect steam stripper removal efficiency include feed concentration and condensate tank temperature and pressure (Ref. 6).

C. OPERATING CHARACTERISTICS

1. Process Inputs/Outputs

Steam stripping is used to remove gases or volatile organics from a dilute wastewater stream. The input to the process is a wastewater stream containing dissolved gases or volatile organic compounds and the outputs are a concentrated vapor or liquid solution containing most of the gases or volatile organics and a very dilute treated wastewater stream containing only very small amounts of dissolved gases or volatile organics.

2. Description of Equipment

The equipment required for steam stripping (as shown in Figure 1) is nearly the same as that required for conventional fractional distillation (i.e., packed column or tray tower, reboiler, reflux condenser and feed tanks and pumps). In steam stripping, however, there are several differences. A heat exchanger is used for heating the feed entering the column and cooling the stripped wastewater leaving the column. Also, the reboiler is often an integral part of tower body rather than a separate vessel.

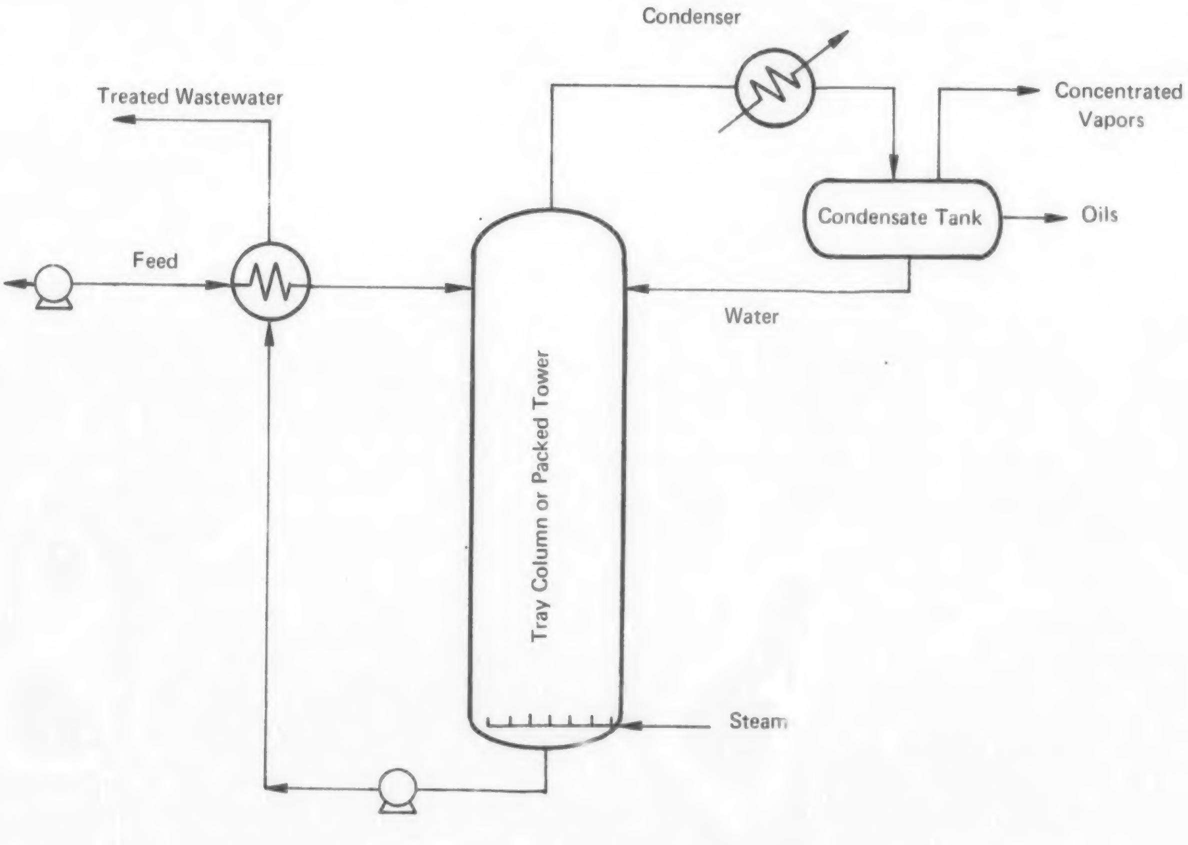
Condenser
Treated Wastewater
Concentrated Vapors
Condensate Tank
Oils
Feed
Water
Tray Column or Packed Tower
Steam

FIGURE 1 TYPICAL STEAM STRIPPING SYSTEM

3. Process Operation

Steam stripping is usually conducted as a continuous operation in a packed tower or conventional fractionating distillation column (bubble cap or sieve tray) with more than one stage of vapor/liquid contact. The preheated wastewater from the heat exchanger enters near the top of the distillation column and then flows by gravity countercurrent to the steam and organic vapors (or gas) rising up from the bottom of the column. As the wastewater passes down through the column, it contacts the vapors rising from the bottom of the column that contain progressively less volatile organic compound or gas until it reaches the bottom of the column where the wastewater is finally heated by the incoming steam to reduce the concentration of volatile component(s) to their final concentration. Much of the heat in the wastewater discharged from the bottom of the column is recovered in preheating the feed to the column.

Reflux (condensing a portion of the vapors from the top of the column and returning it to the column) may or may not be practiced depending on the composition of the vapor stream that is desired. By using a reflux in sour water stripping, the concentration of the hydrogen sulfide and ammonia in the vapor stream leaving the column can be increased, reducing the water load to the sulfur recovery unit or incinerator. This increased concentration of stripped gases can, however, lead to ammonium sulfide deposits in the vapor duct and corrosion unless the vapor lines are adequately insulated and heated (Ref. 7).

In the case of pulp mill condensate stripping, the "foul oil" and water vapor are condensed from the vapors leaving the stripping column, the oil and water are separated by gravity, and the saturated water returned to the stripper. The "foul oil" (which contains turpentine) is sent to turpentine recovery.

Uncondensed vapor (containing sulfides, mercaptans, methanol, and water) is sent to the incinerator or lime kiln to be burned.

Although many of the steam strippers in industrial use introduce the wastewater at the top of the stripper, there are advantages to introducing the feed to a tray below the top tray when reflux is used.

Introducing the feed at a lower tray (while still using the same number of trays in the stripper) will have the effect of either reducing steam requirements (due to the need for less reflux) or yield a vapor stream richer in volatile component (Ref. 6). The combination of using reflux and introducing the feed at a lower tray will increase the concentration of the volatile organic component beyond that obtainable by reflux alone. (As indicated earlier in this text, increasing the organic vapor concentration decreases the water load on the sulfur recovery unit or incinerator.)

D. EQUIPMENT AND MATERIALS

A description of the equipment required for steam stripping and its operation was presented in the previous section. The choice of materials of construction for steam stripping systems depends on the operating pH and the presence (or absence) of corrosive ions present (i.e., sulfides, chlorides). In a single-column sour-water steam stripper, the high pH, from the presence of ammonia, allows mild steel to be used. If the sour water is stripped in two columns (H_2S removed in one and HN_3 removed in the other) the material of construction of the unit in which the H_2S is removed should be alloy steel or alloy clad steel.

III. APPLICATIONS TO DATE

Steam stripping is used in both industrial chemical production (for recovery and/or recycle of product) and in industrial waste treatment. Three common examples of product recovery by steam stripping are ammonia recovered for sale as ammonia or ammonium sulfate from coke oven gas scrubber water, sulfur from refinery sour water, and phenol from water solution in the production of phenol. More recently, steam stripping has been applied to wastewater treatment. Some of these newer applications include removal of phenols, mercaptans, and chlorinated hydrocarbons from wastewater.

A. CURRENT APPLICATIONS TO INDUSTRIAL CHEMICAL PRODUCTION

1. Ammonia from Coke Oven Gas Scrubber Water

Ammonia stripping as practiced in recovering ammonia from coke oven gas is a steam distillation operation in which steam is used to strip (remove) dissolved ammonia from water. The operating principles are based on the high partial pressure of ammonia over alkaline solutions and the equilibrium between the ammonia and ammonium ions in the liquid phase. In order for the ammonia to be freed from the sulfate, chloride and other anions present, the pH must be on the alkaline side. The desirable pH range of 10-11 is normally obtained by addition of lime. This high pH also results in a low vapor pressure for the cyanides and phenols present in the scrubber water preventing their release during the ammonia stripping operation.

The ammonia still in Figure 2 is typical of those used in the semi-direct ammonia recovery process employed for recovery of the ammonia produced in coke ovens. About 85% of all coke ovens in the United States employ this method (Ref. 8).

The waste stream is introduced at the top of the free still where it is contacted by steam introduced at the bottom of the column. Lime, which is introduced below the free still into the so-called lime leg, is necessary to react with the ammonium salts and drive the reaction equilibrium to ammonia gas. Thus, dissolved NH_3 is stripped in the free still area while NH_4 is converted to NH_3 in the lime leg. The high pH solution in the lime leg overflows into the fixed leg where the remaining NH_3 is removed. Ammonia-saturated gas exits from the still and the stripped scrubber water is sent to a dephenolizer where the phenol is removed by steam stripping at a lower pH or by solvent extraction.

Table 1 presents data reported in the literature of ammonia removal efficiency for steam stripping of coke oven gas scrubbing water.

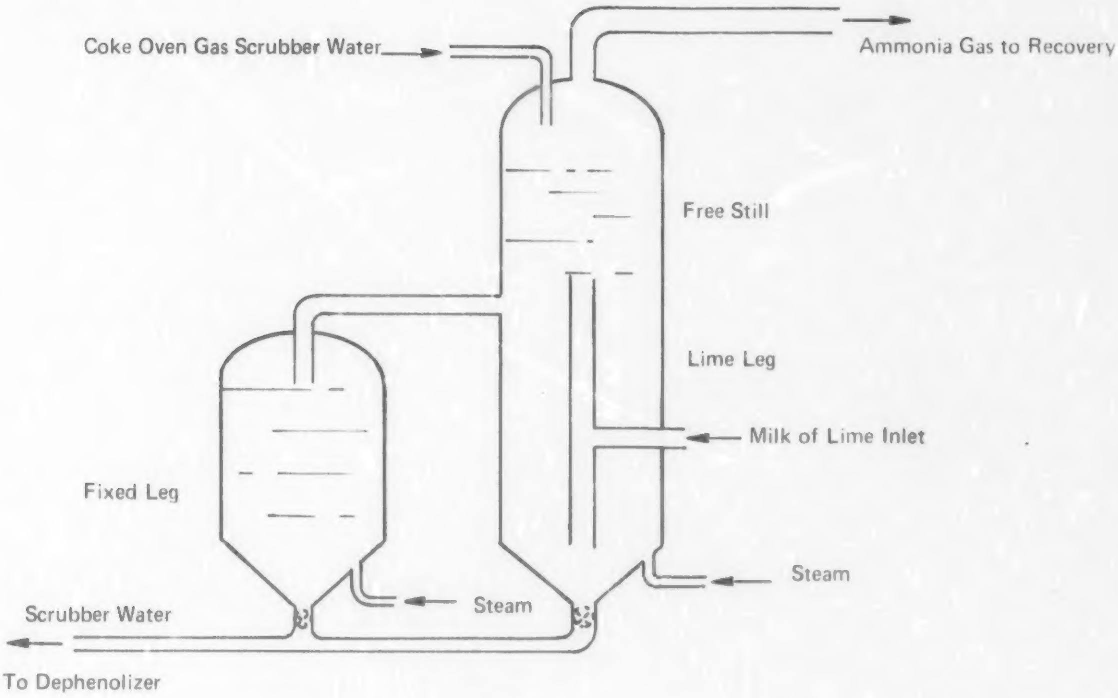
Coke Oven Gas Scrubber Water
Ammonia Gas to Recovery
Free Still
Lime Leg
Milk of Lime Inlet
Fixed Leg
Steam
Steam
Scrubber Water
To Dephenolizer

FIGURE 2 AMMONIA STRIPPING OF COKE OVEN GAS SCRUBBER WATER

TABLE 1

APPROXIMATE COMPOSITION OF CRUDE LIQUORS TO AND FROM THE AMMONIA STILL

(mg/liter, except pH)

Liquor	To Ammonia Still	From Ammonia Still, in Plant Having No Dephenolizer
Total ammonia	7000	0.04- 2.5
Free ammonia	4000	0 - 0.04
Fixed ammonia	3000	0 - 2.5
Cyanide, as HCN	20- 100	10 - 100
Chloride	1100-6000	1100 -5000
Sulfate	150-1000	150 -1000
Phenols	400-3000	400 -2500
pH	–	9 - 12.5
BOD	–	2000 -4000

Source: Ref. 9.

2. Sulfur and Ammonia from Refinery Sour Water

Until recently, little attention was given to optimizing the design of sour water strippers for ammonia removal since the prime concern was removal of H_2S (Ref. 6). The H_2S removed in the stripper was sent to a sulfur plant for recovery or was incinerated. Operation of a (steam) sour water stripper in a pH range of 6-7 at 110°C will result in over 99% removal of H_2S, but very little (less than 30% removal) of NH_3. With more stringent effluent requirements, more efficient removal of NH_3 is required. By increasing the pH to between 8 and 9, NH_3 removal is increased to between 85 and 95% but H_2S removal efficiency drops to about 98% (Ref. 1). With a further increase in pH the H_2S removal efficiency will drop off sharply. Since the concentration of both H_2S and NH_3 in the sour water feed to the stripper are typically between 2,000 and 10,000 ppm, it is important to remove both of these components. Two solutions for more efficient NH_3 and H_2S removal have been proposed. One solution proposes introducing caustic soda near the bottom of the stripper to increase the pH in this zone of the stripper and release NH_3 after the H_2S has been removed in the upper section of the stripper (Ref. 6).

The second solution, which has been proven industrially, allows separate removal of the H_2S and NH_3 in two stripping towers at different pH's. The following stream compositions are reported for one such system (Ref. 4).

	ppm By Weight		
Stream	**Ammonia**	**Hydrogen Sulfide**	**Water**
Stripped Water	<50	<5	Balance
Ammonia	Balance	<5	–
Hydrogen Sulfide	<50	Balance	<5000

Since the input stream to the stripper in this plant contains about 15-30,000 ppm ammonia and 35-70,000 ppm hydrogen sulfide, this represents over 99.7% removal of ammonia and about 99.99% removal of hydrogen sulfide. In this particular system, the steam is supplied by boiling the wastewater in the bottom of the column using an external heat exchanger rather than injecting live steam into the wastewater in the bottom of the column.

The advantage of this system over a conventional single-stage stripper is the complete separation of the H_2S and NH_3, while the disadvantage is the higher capital cost. The columns used for sour water steam stripping range in size from 2 to 10 feet in diameter and 20 to 40 feet in height. Feed rates to the column range from about 40 to 250 gpm.

3. Phenol from Phenol Production Process Water

In the production of phenol by the sulfonation and chlorobenzene processes, an aqueous phenolic process stream is generated from which the phenol is recovered by steam distillation. The phenol in this case is removed from the aqueous stream as a phenol/water azeotrope.

4. Ammonia from Nitrogen Fertilizer Manufacture

Packed or tray columns are used for contacting steam with nitrogen fertilizer process condensate (from evaporators and crystallizers) to strip ammonia which is then condensed with the steam and recovered by distillation.

B. CURRENT APPLICATIONS TO INDUSTRIAL WASTE TREATMENT

As described in the previous section, petroleum refinery "sour water" wastewater is treated by steam stripping to remove (and recover) ammonia and hydrogen sulfide.

1. Steam Stripping of Phenol Plant Effluent

The treatment system at Dow Chemical Company's Midland, Michigan, plant includes a steam stripping section that reduces the phenol content to between 150-750 ppm before subsequent treatment by carbon adsorption.

2. Steam Stripping of Vinyl Chloride Monomer

B.F. Goodrich has recently announced the development of a continuous steam stripping system for removing vinyl chloride monomer from suspension resins of polyvinyl chloride (Ref. 10).

3. Steam Stripping of Kraft Mill Condensate

Kraft mill condensates are steam stripped to remove BOD (mainly methanol) and TRS (total reducible sulfur) compounds at the Escanaba, Michigan, Pulp and Paper Mill of Mead Corp. (Ref. 11). The condensates are steam stripped in 24 tray bubble cap, 7-foot diameter x 53-foot high, distillation column at a rate of about 200 gpm. The preheated wastewater flows downward through the column passing countercurrent to the steam and volatile organic vapors passing upward through the column. The vapors from the top of the column are partially condensed to remove "foul oil" (mostly turpentine) and water vapor while allowing most of the methanol and TRS compounds to pass through as vapors. These vapors of methanol and TRS (and also some water vapor) are sent to the lime kiln or an incinerator to be burned. The condensed water and "foul oil" are decanted, the "foul oil" sent to turpentine recovery and the condensed water returned to the top of the stripper.

The steam stripper wastewater from the bottom of the stripper used to be discharged to the biological wastewater treatment, but is now recycled to the brownstock washers. Thus, there is no direct discharge to the environment from this steam stripping system.

The efficiency of this steam stripping system is summarized below:

	Kraft Mill Condensates	
Component	**Before Stripping**	**After Stripping**
BOD_5	10,000 ppm	2,500 ppm
Methanol	0.8% vol	0.2% vol
TRS	20,000 ppm	100-200 ppm

To treat 200 gpm (12,000 gallons/hr) of Kraft Mill condensates in this system requires about 10,000 lbs/hr of steam.

4. Steam Stripping of Light Chlorinated Hydrocarbon Production Wastewater

The Robert S. Kerr Environmental Research Laboratory is currently sponsoring a research program studying the removal of low-molecular-weight chlorinated hydrocarbons from process wastewater by steam stripping. Removal efficiencies of up to 90% for waste streams containing 3,000-6,000 ppm chlorinated hydrocarbons have been obtained (Ref. 3).

5. Steam Stripping of Low-Level Radioactive Wastes

The test results shown in Table 2 were obtained in a pilot plant steam stripper processing low level radioactive waste. About 15% of the waste stream was boiled off as steam in the stripper (Ref. 12).

TABLE 2

CONCENTRATIONS OF TRIBUTYL PHOSPHATE, HYDROCARBON DILUTE, AND AMMONIA IN FEED AND STRIPPER BOTTOMS (mg/liter)

	Feed	Stripper Bottoms
Tributyl Phosphate	24-65	0.5-1.2
Hydrocarbon Diluent	5-23	1.0-2.2
Ammonia	16-22	0.1-0.8

Source: Ref. 12.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

The major energy requirement in this unit operation is the steam requirement which, in turn, is related to process efficiency. Table 3 summarizes the steam requirements and removal efficiencies for a series of steam stripping applications.

TABLE 3

TYPICAL STEAM STRIPPER STEAM REQUIREMENTS AND EFFICIENCIES

Application		Steam Requirements (lbs per gallon)	Removal Efficiency
Refinery Sour Water (Single Stripper)	(6 trays)	0.6	98.9% H_2S 87.3% NH_3
	(6 trays)	0.9	99.0% H_2S 93.0% NH_3
	(12 trays)	1.2	99.8% H_2S
	(12 trays)	1.8	99.85% H_2S 95.0% NH_3
	Packed Tower	1.5	98% H_2S 93% NH_3
		2.0	98.5% H_2S 96% NH_3
Kraft Mill Condensate	(24 trays)	0.8	75% Methanol 99% TRS

Source: Refs. 1, 11.

In general, data on existing systems for NH_3, H_2S, phenol, methanol, TRS stripping indicate little increase in efficiency beyond 2.0-2.5 lb stripping steam (2.5-3.0 lb total steam including preheat) per gallon of wastewater.

For a 200 gpm steam stripper, steam requirements at 2 lb/gal wastewater would be 1,400 lb/hr steam and electrical energy requirements would be about 20 kWh/hr.

B. ENVIRONMENTAL ISSUES

The steam stripped volatiles are usually processed further for recovery or incinerated. If the stripped volatiles contain sulfur and are incinerated, the impact of SO_2 emissions must be considered. The impact of the stripped wastewater would depend on the quantity and type of residual volatile organics remaining in the stripped wastewater. Land requirements for this treatment system are small and there are generally no discharges except for the treated wastewater.

C. ECONOMIC ANALYSIS

1. Capital Investment

The equipment shown in Table 4 would be required for a (continuous) steam stripping system for a feed rate of 200 gpm.

TABLE 4

CAPITAL INVESTMENT FOR A 200 GPM STEAM STRIPPER
(all equipment 304 stainless steel)

	Purchased Equipment (Jan. 1976)
Feed Pump 200 gpm @ 130 ft head	$ 4,000
Feed Pump 200 gpm @ 60 ft head	1,800
Feed Heat Exchanger 800 sq ft	20,000
Distillation Column 24 trays, 6 ft diam. x 60 ft	140,000
Condenser – 400 sq ft	12,000
Condensate Tank – 1000 gal	4,000
Total Purchased Equipment	$181,800
Total Capital Investment	$850,000

Source: Arthur D. Little, Inc., estimates.

In mild steel, the capital investment for this single-column, 200-gpm steam stripper would be about $500,000.

The total capital investment reported for a two column 200-gpm system (Chevron WWT process) in 1972 was $1,250,000 (Ref. 4). In January 1976 (using the CE plant cost index), this system would cost about $1,700,000.

2. Operating Cost

The estimated operating cost for a 200-gpm steam stripping system is presented in Table 5.

TABLE 5

OPERATING COST FOR A 200 GPM SOUR WATER STEAM STRIPPER

Waste Stream: 200 gpm sour water containing 5% by wt $(NH_4)_2S$
Operation: 350 days/yr, 24 hr/day
Capital Investment: $850,000 – 100 MM gal/yr

Variable Costs	**$/Unit**	**Units/ 1000 Gal Wastewater**	**$/ 1000 Gal Wastewater**	**Annual Cost ($)**
Operating Labor (2m-h/shift)	12.00/MH	–	0.25	25,200
Steam	4.00/1000 lb	2000 lb	8.00	–
Electrical Energy	0.02/kWh	1.7 kWh	0.03	–
Cooling Water	0.08/1000 gal	12,000 gal	0.96	–
Maintenance			0.42	42,500
Total Variable Cost			$ 9.66	
Fixed Costs				
Capital Recovery (10 yrs at 10%)			1.38	138,000
Taxes and Insurance (at 2% cap. inv./yr)			0.17	17,000
Total Fixed Costs			$ 1.55	
Total Operating Cost			$11.21 (1000 gal wastewater)	

Source: Arthur D. Little, Inc., estimates.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

With increasingly more stringent wastewater guidelines, the use of steam stripping will become more widespread. Even now this unit operation is being investigated in many industries as a technique for reducing the concentration of volatile organic compounds in wastewater streams either to allow direct reuse or discharge of the wastewater stream or to reduce the load of volatile organics on subsequent waste treatment processes (i.e., ion exchange or biological treatment). Although some present applications of this process have a near breakeven operating cost because of recovered by-products (i.e., sulfur from refinery "sour water," it is likely that most of the future applications will not recover enough in the way of by-products to offset the operating cost. Its specific application will, therefore, depend on its efficiency compared with other wastewater treatment processes.

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B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD

Facilities that practice steam stripping as a method of wastewater treatment include:

Petroleum Refineries – Sour water stripping
Coke Producers – Coke oven gas scrubbing water strippers
Phenol Producers – For wastewater treatment and product recovery
Ammonia Fertilizer – For wastewater treatment and product recovery

The first North American kraft mill to use full-scale steam stripping of condensate was:

Escanaba Pulp and Paper Co.
Division of Mead Corporation
Escanaba, Michigan 49829

ULTRAFILTRATION

Prepared by

James D. Birkett

I. CONCLUSIONS AND RECOMMENDATIONS

Ultrafiltration is a membrane separation system capable of segregating dissolved or suspended species from a liquid stream on the basis of size. These species may range from large organic molecules (mol. wt. $\sim$ 1000) to larger agglomerations.

Ultrafiltration presently has commercial applicability in several industrial situations and is increasing its markets. There are several suppliers of equipment offering a wide range of designs and membrane materials.

Operating costs, about 0.5-1¢ per gallon, and capital costs, about $1-4 per gpd capacity are higher than those of reverse osmosis to which ultrafiltration is related, due to small unit sizes, shorter equipment life, and higher pumping costs. Reclamation of valuable components may be necessary to justify these higher costs.

Ultrafiltration is uniquely capable of making certain separations especially from concentrated streams. However, each installation must be carefully piloted as the system design and determination of operating parameters is critical.

II. PROCESS DESCRIPTION

Ultrafiltration is a membrane filtration process which separates high molecular weight solutes or colloids from a solution or suspension. The process has been successfully applied to both homogeneous solutions and colloidal suspensions which are difficult to separate practically by other techniques. To date, commercial applications have been entirely focused on aqueous media.

The basic principle of operation of ultrafiltration is illustrated in Figure 1. Flowing by a porous membrane is a solution containing two solutes: one of a molecular size too small to be retained by the membrane, and the other of a larger size allowing 100% retention. A hydrostatic pressure, typically between 10-100 psig, is applied to the upstream side of the supported membrane, and the large-molecule solute or colloid is retained (rejected) by the membrane. A fluid concentrated in the retained solute is collected as a product from the upstream side, and a solution of small-molecule solute and solvent is collected from the downstream side of the membrane. Of course, where only a single solute is present and is rejected by the membrane, the liquid collected downstream is (ideally) pure solvent.

Retained solute (or particle) size is one characteristic distinguishing ultrafiltration from other filtration processes. Viewed on a spectrum of membrane separation processes, ultrafiltration is only one of a series of membrane methods which can be used. For example, reverse osmosis, a membrane process capable of separating dissolved ionic species from water, falls further down the same scale of separated particle size. In Figure 2, that size spectrum is shown as a function of filtration flux. At the small-molecule/low-flux end of the spectrum lies the commercial cellulose acetate reverse osmosis membrane, with the capability of retaining hydrated sodium and cloride ions. Next come ultrafiltration membranes with pores that cover a size range of about 10^{-3} to 10^{-2} microns (10-100Å) with filtration fluxes of about 0.5 to 10 gallons/sq ft/day/psi of pressure driving force. Microporous filters capable of virus and bacteria retention cover the pore size range of about 0.01 to 1.0 microns, with fluxes of 10-1000 gallons/sq ft/day/psi Δp.

In a sense, any reverse osmosis membrane also ultrafilters although perhaps at very low flux states. In turn, some ultrafiltration membranes may exhibit a slight degree of retention of ionic species.

Ultrafiltration membranes are asymmetric structures, possessing an extremely thin selective layer (0.1-1.0 microns thick) supported on a thicker spongy substructure. Controlled variation of fabrication methods can produce membranes with desirable retentive characteristics for a number of separation applications. Indeed, it has become possible to tailor membranes with a wide range of selective properties. For example, tight membranes can retain organic solutes of 500-1000 mol wt while allowing passage of most inorganic salts. Conversely, loose membranes can discriminate between solutes of 1,000,000 vs. 250,000 mol wt.

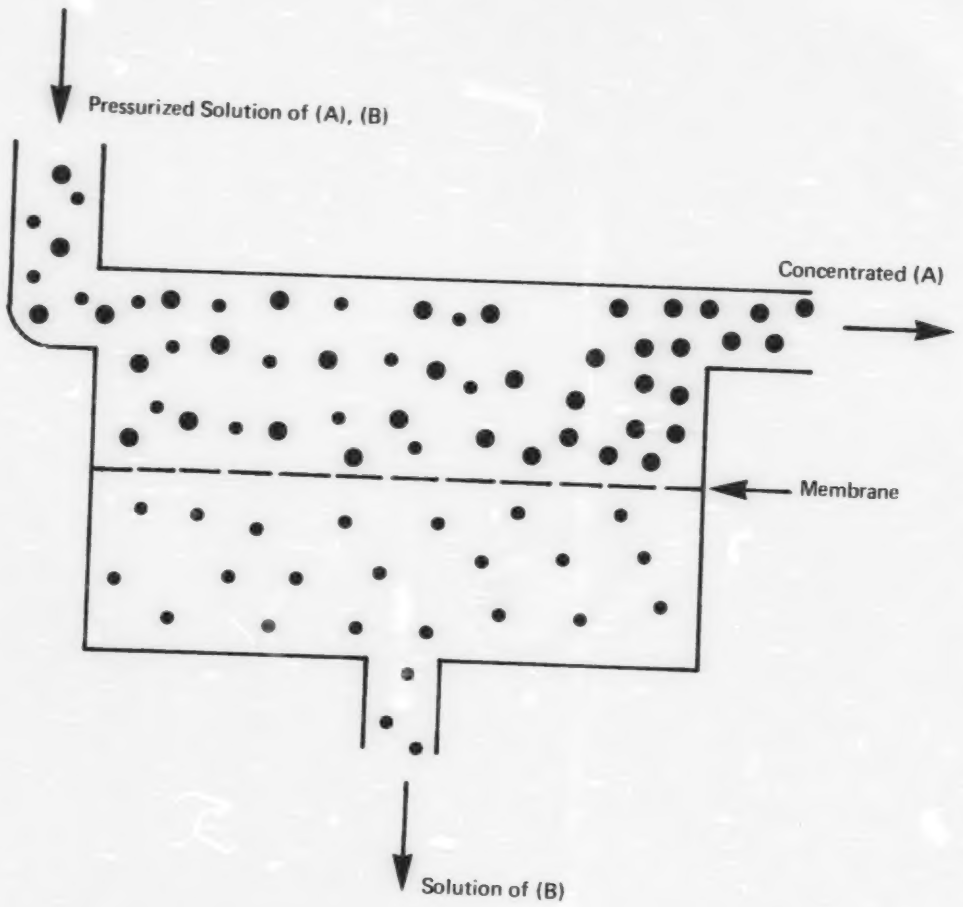
Pressurized Solution of (A), (B)
Concentrated (A)
Membrane
Solution of (B)

FIGURE 1 SCHEMATIC DIAGRAM OF MEMBRANE ULTRAFILTRATION PROCESS

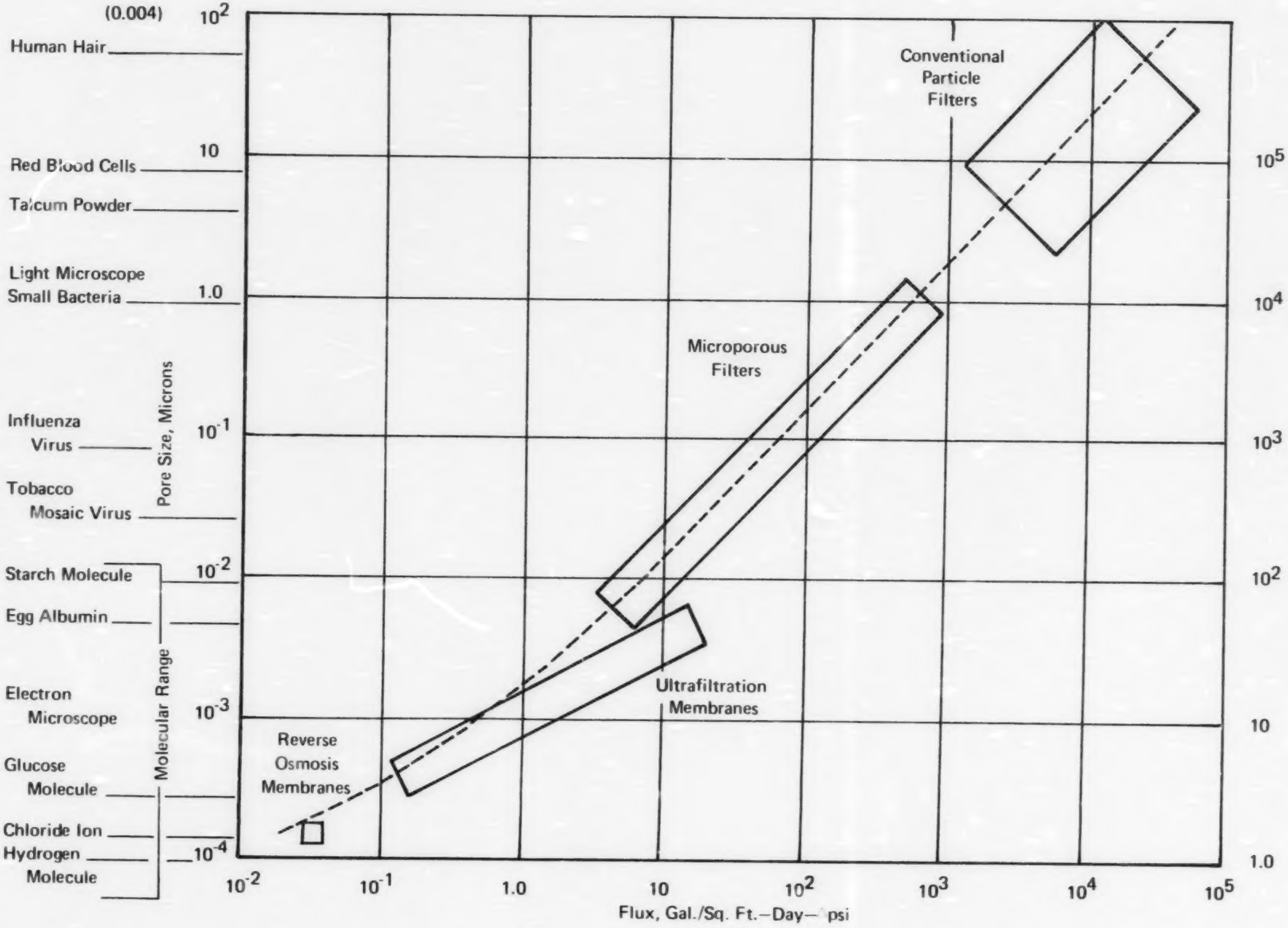

FIGURE 2 PORE SIZE VS. FLOW RATE FOR SEPARATION MEDIA

Ultrafiltration membranes are different from so-called "solution – diffusion" membranes, which have been the subject of study for a wide variety of gas and liquid-phase separations. The latter group possesses a permselective structure which is non-porous, and separation is effected on the basis of differences in solubility and molecular diffusivity within the actual polymer matrix. Reverse osmosis membranes generally fall into this category.

Membranes can be made from various synthetic or natural polymeric materials. These range from hydrophilic polymers such as cellulose, to very hydrophobic materials such as fluorinated polymers. Polyarylsulfones and inorganic materials have been introduced to deal with high temperatures and pH values.

Membranes of this type are in many respects similar to reverse osmosis membranes except for the openness of their pores. Other forms and materials are available as well, including porous zirconia, deposited on a porous carbon substrate and on a porous ceramic tube. The latter two systems, while more expensive than the former, are capable of use to very high pH values and temperatures.

III. APPLICATIONS TO DATE

A. INDUSTRIAL APPLICATIONS

The properties of ultrafiltration membranes lead to a range of applications quite distinct from those of conventional filtration. Where solutes are being separated from solution, ultrafiltration can serve as concentration or fractionation process for single-phase liquid streams. Thus, ultrafiltration competes with adsorptive and evaporative separation processes, and has the potential for broader applicability than conventional filtration. Usually, it will not perform the entire separation task, because it produces a concentrated rather than a solvent-free product, and the concentrate requires further processing if a pure solute is to be recovered.

Applications of ultrafiltration may fall into one of three categories:

- Concentration, where the desired component is rejected by the membrane and taken off as a fluid concentrate;
- Fractionation, for systems where more than one solute are to be recovered, and products are taken from both the rejected concentrate and permeate;
- Purification, where the desired product is purified solvent.

Table 1 presents a summary of major existing ultrafiltration applications. Also shown is the function of ultrafiltration processing for the specific application.

TABLE 1

COMMERCIAL APPLICATIONS OF ULTRAFILTRATIONS

Application	Function
Electrocoat Paint Rejuvenation and Rinse Water Recovery	Fractionation
Protein Recovery From Cheese Whey	Concentration and Fractionation
Metal Machining, Rolling, and Drawing – Oil Emulsion Treatment	Purification
Textile Sizing (PVA) Waste Treatment	Fractionation
Electronics Component Manufacturing Wash Water Treatment	Purification
Pharmaceuticals Manufacturing Sterile Water Production	Purification

Table 2 gives a summary of developmental applications of ultrafiltration. These represent areas which are likely to be commercial within the next 5 years. Table 3 indicates firms currently active and the nature of their technology.

TABLE 2

DEVELOPMENTAL APPLICATIONS OF ULTRAFILTRATION

Application	Function
1. Dye Waste Treatment	Concentration and Purification
2. Pulp-Mill Waste Treatment	Concentration and Purification
3. Industrial Laundry Waste Treatment	Purification and Fractionation
4. Protein Recovery from Soy Whey	Concentration
5. Hot Alkaline Cleaner Treatment	Fractionation and Purification
6. Power-plant Boiler Feedwater Treatment	Purification
7. Sugar Recovery from Orange-juice Pulp	Fractionation
8. Product Recovery in Pharmaceutical and Fermentation Industries	Concentration
9. Colloid-free Water Pollution for Beverages	Purification

TABLE 3

CURRENT TECHNOLOGY

Company	Geometry	Membrane Type
Abcor	1" diameter tubular membranes and spiral wound flat membranes	Originally cellulose acetate; now, other materials which are pH and temperature resistant
Dorr Oliver	Multiple flat plate	Polyelectrolyte complex (developed by Amicon)
Romicon*	Narrow channel tubular (flat sheet membrane); also hollow fibers	Dynel^R (acrylic), cellulose acetate, Nomex^R (nylon) polyelectrolyte complexes, others
Union Carbide	1/4" tubes	Zirconium oxide on carbon
Millipore	Multiple plate and screen cartridge	Cellulose acetate and others more solvent resistant
Osmonics	Spiral-wound modules, 2" and 4" diameter	Cellulose acetate and polyarylsulfone
Selas	Tubular	Zirconium oxide deposited in-situ on porous ceramic

*Joint venture of Rohm & Haas and Amicon.

B. APPLICABILITY OF ULTRAFILTRATION TO HAZARDOUS WASTES

Among the actual commercial applications of ultrafiltration listed in Table 1, the first four involve treatment of industrial streams of high potential pollutant concentrations.

1. Electrocoat Paint Rejuvenation and Rinse Water Recovery

Electrocoating is a painting and coating process for metallic parts. The paint is a colloidal suspension of charged pigment particles in high concentration, which migrate to the metal part of the surface under an electric potential applied between the part and the paint bath tank wall. After periods of use, impurities build up in the paint which render it useless, and it must be sewered. As a wastewater, it cannot be effectively treated in a sewage treatment plant, and it therefore contaminates the treatment plant effluent with organics and color. In addition, water from rinsing the excess paint from the coated part is also sewered in very high volumes, and it similarly represents an untreatable hazard.

Ultrafiltration is now used in most electrocoat painting plants in two ways. First, ultrafiltration can often fractionate the paint from impurities by retaining the colloidal particles and allowing the dissolved impurities to pass through the membrane. Thus it extends the life of a paint bath, and drastically reduces the pollution caused by paint bath discharge. Second, ultrafiltration can recover the colloidal paint from rinsewaters, thereby eliminating pollution from the rinsewater effluent, and recovering paint for return to the paint bath. This combined process has been the most successful application of ultrafiltration in industry to date. It is invariably the process of choice and the market is near saturation.

2. Protein Recovery from Cheese Whey

Cheese whey is produced in all cheese-making operations. It contains about 1% soluble protein, and several percent lactose, the principal organic pollution contributor. In addition, there are smaller amounts of lactic acid, some amino acids, and salts. Whey is a greenish, somewhat viscous fluid with a BOD of about 60,000. As such, it is a severe water pollution problem, and much of it is discharged directly into streams.

Ultrafiltration effects a fractionation by retaining and concentrating soluble protein, and allowing passage of lactose and other small-molecules through the membrane. The protein can be recovered as valuable by-product. The ultrafiltration effluent product is still high in BOD, most of which is attributable to the lactose. However, with removal of protein, the lactose and a purified water stream can be recovered by evaporation or by reverse osmosis. Thus, by separating a high-value by-product, ultrafiltration helps pay for the entire pollution-control process.

3. Metal Machining-Oil Emulsion Treatment

Metal cutting, rolling, and drawing oils are used as dilute emulsions to lubricate metal-working machines. The spent lubricant is heavily contaminated with metal fines and dirt. In the past, the spent emulsion has either been trucked away for disposal or sewered directly at the plant.

Ultrafiltration can concentrate the dirty spent emulsion, increasing the oil and solids contents from several tenths of a percent to higher than 50%. Thus, over 95% of the water can be removed and sewered or reused safely, and a small-volume concentrate can be disposed of by other means. The cost of incineration drops dramatically as the oil concentration is increased to the point where the solution will support combustion.

Problems can arise, however, when the oil is kept in suspension by a lower molecular weight emulsifying agent. This agent may permeate the membrane (increasing the BOD of the permeate) and its absence from the concentrate permits the oil to agglomerate and block the membrane. For this reason "tighter" membranes, more like an RO membrane may be needed to reject the agent.

4. Textile Sizing (Polyvinyl Alcohol) Waste Treatment

Soluble polyvinyl alcohol is now frequently used as textile fiber sizing. After production of the fabric from fiber, the sizing is washed away, producing high pollutant-content wastewater.

Ultrafiltration has been successfully used to retain the PVA while producing purified water for disposal or recycle. Operation at high temperatures (> 66°C) permits significant energy savings as the hot permeate is recycled.

In Table 2, the first five items listed are potential applications of ultrafiltration to hazardous materials. These are:

(1) dye waste treatment;

(2) pulp-mill waste treatment (both bleach-plant effluent and decker effluent);

(3) industrial laundry wastes;

(4) soy whey, and

(5) hot alkaline cleaner.

In each case, similar to the existing applications described above, ultrafiltration can retain the polluting component, producing a water effluent suitable for disposal or recycle. Exceptions are soy whey, which has a contaminated ultrafiltrate similar to cheese whey and would require further treatment such as evaporation to produce a harmless pure water effluent, and alkaline cleaners in which the permeate would still be strongly alkaline, but free of dirt, oils, and fines.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Electrical energy is the only energy input required for ultrafiltration. It supplies the pumping power required to maintain good flow rates at the operating pressures, usually 60-200 psi. In certain instances, energy costs may run as high as 30% of total direct operating costs but are generally less.

B. ENVIRONMENTAL IMPACTS

Since ultrafiltration involves no chemical conversion, residues from the process are typically a concentrate of the undesirable or hazardous components. The process generally serves to provide a greatly reduced volume of the hazardous waste, but does not inherently provide any elimination of the waste. The noteworthy exceptions, of course, are those cases where a pollutant can be recovered as a valuable by-product, such as soluble whey proteins or PVA sizing for recycle. Otherwise, organic concentrates require further processing for ultimate disposal, such as additional concentration and incineration.

In the case of some fractionation applications of ultrafiltration, the concentrate and ultrafiltrate require further processing before end disposal occurs. For example, in cheese whey treatment, the lactose content of the ultrafiltrate is far too high to permit sewering, and additional processing steps must be taken before the stream is ready for disposal.

C. ECONOMIC ANALYSIS

Both capital and operating costs for ultrafiltration are strongly dependent on the specific application and the capacity of the system. There is no typical model. For large plants (25,000 gpd), a rough figure for capital cost is $1-$4 per gpd of capacity. Operating costs, including depreciation of capital, may run as high as 0.5-1¢ per gallon ($5-$10 per 1000 gallons). As much as one-third of the operating costs may be required for energy of pumping viscous feeds at high velocity and shear rates.

Although these costs appear high when compared directly to the costs of other membrane processes, it must be remembered that ultrafiltration generally operates at lower total throughputs and considerably higher solute concentrations, than reverse osmosis. Special construction costs are encountered when dealing with the food or drug industries, and membrane life may be short due to rigorous operating conditions or cleaning requirements. Coupled with the economics of reuse of salvaged materials, the costs are frequently acceptable.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Ultrafiltration has genuine utility in certain waste treatment applications, generally those involving the separation of high molecular weight solutes or suspended materials from an aqueous stream. Under optimum conditions it can produce a recyclable concentrate and "innocuous" permeate. However, costs may be high (both operating and capital) and operating conditions and plant design must be carefully tailored to the application. Careful piloting is a prerequisite. Nonetheless, ultrafiltration has demonstrated unique capabilities in oil/water separation, electropaint recovery, and the dairy processing industry, and it is certain that new applications will continue to be developed.

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7. Rey, G., Lacy, W.J., and Cywin, A., "Industrial Wastes Reuse: Future Pollution Solution," Environmental Sciences and Technology, September 1971, Vol. 5, No. 9, pp. 760-765.

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B. PEOPLE/ORGANIZATIONS EXPERIENCED IN THE FIELD

Further information regarding recent developments in ultrafiltration technology may be obtained from the manufacturers previously cited in Table 3. In addition, applications of ultrafiltration to industrial waste treatment have been followed closely by Professor Craig Brandon of Clemson University under EPA sponsership.

ZONE REFINING

Prepared by

Joseph P. Tratnyek

I. CONCLUSIONS AND RECOMMENDATIONS

For small amounts of material zone refining (zone melting) is an efficient purification technique which has been used to obtain high-purity organic and inorganic materials. However, except for its commercial use in the semiconductor industry, it has remained a laboratory tool. No industrial waste streams are currently treated by zone refining.

In general, zone refining is a costly operation in both time and money and is presently limited to treatment of small batches of material (up to 10 kg.) There is some industrial interest in developing zone refining for processing large amounts (> 10 kg) of high quality organic materials, but heat transfer problems and slowness of the operation have hindered progress. Energy costs would be high. Large heat losses make zone refining prohibitive for the metals industry.

Generally the process is not useful for viscous materials such as tarry materials and glasses. For liquid stream, e.g., salt water, zone refining has been proposed but is impractical. Complex mixture processing would be difficult with zone refining, and would require a multistage operation. A cost of 25¢/lb might be added to processing organic materials and as much as $10/lb for metals.

Although zone refining may be applicable for recycling of high value substances, it is unlikely to have broad application to industrial waste materials in large quantity. Significant developments applicable to waste treatment are unlikely within the next five years.

In spite of a potential capability for treating some wastes and producing high purity separations, zone refining is unlikely to become a practical, operational waste treatment system in the near future. It will remain inherently slow and costly. We recommend zone refining not be considered for waste treatment.

II. PROCESS DESCRIPTION

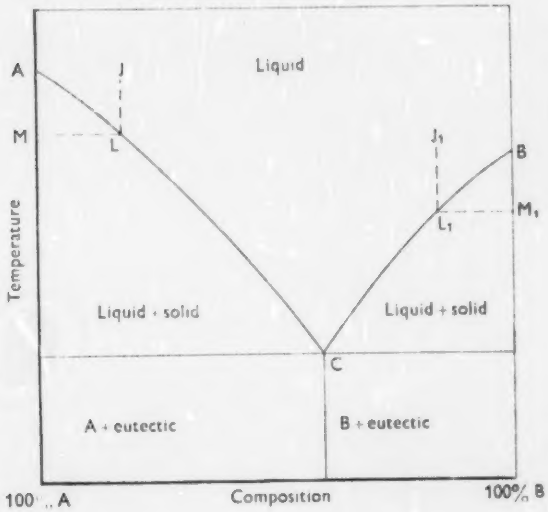
A. BACKGROUND

Zone refining is a modification of the classical purification technique of fractional crystallization. Pfann (Ref.1) has written the standard text which describes in detail the history, principles, and development of zone refining since he first applied the technique to germanium in 1952. Since that time numerous zone-refining studies have been reported. In spite of the large amount of literature on the subject, commercial application has been slow since its advent on the industrial scene over 20 years ago. Growing high purity single crystals for research and the semiconductor industry remains the sole industrial application at present.

B. UNDERLYING PRINCIPLES

Details of the principles of zone refining and the zone refining operation and problems are reported adequately in the literature (Refs. 1-5,9). Gouw and Jentoft have compared the efficiencies of normal freezing, column crystallization and zone melting (Ref. 8).

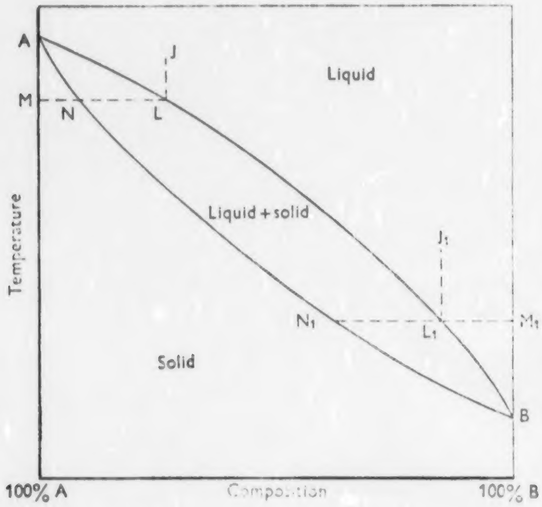
When a liquid mixture is cooled, the solid that crystallizes out usually has a composition different from that of the liquid. The purification of substances by zone refining depends on this difference. Two simple types of solid-liquid equilibrium reveal some of the conditions that arise during zone refining. In a system with the phase diagram in Figure 1, the cooling of liquid of composition J will cause crystallization of pure component A when the temperature corresponding to point L is reached. On the other hand, if the original composition corresponds instead to point J_1, the first solid to separate will be pure component B.



Source: Ref. 2.

FIGURE 1 PHASE DIAGRAM FOR A SYSTEM EXHIBITING A SIMPLE EUTECTIC

The behavior of a mixture that forms a series of solids solutions is shown in Figure 2. Here, solid of composition N separates when liquid of composition J cools. This solid is richer in component A than the liquid from which it came, but still contains component B. If the original composition corresponds instead to point J_1, then the solid first deposited will have composition N_1. The solid is thus richer in component A than the liquid from which it has been deposited, whatever the initial composition of the liquid.



Source: Ref.2.

FIGURE 2 **PHASE DIAGRAM FOR A SYSTEM EXHIBITING A SERIES OF SOLID SOLUTIONS**

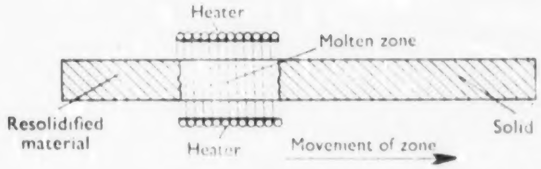
In discussing zone refining of such mixtures, it is convenient to define an "ideal distribution coefficient" (k_1) as the ratio of the percentage of impurity in the solid that is crystallizing to that in the liquid with which it is in equilibrium. When the original composition is J, $k_1 = MN/ML$; when the original composition is J_1, $k_1 = M_1N_1/M_1L_1$. The value of k_1 is thus less than unity for composition J and greater than unity for composition J_1. The same definition of k_1 can be adopted for systems represented by Figure 2, if N is regarded as coinciding with M in that figure. In such systems $k_1 = o$ for liquids of composition J and also for those of composition J_1.

Zone refining is normally used on material already of high purity, and most studies are therefore concerned with points on the phase diagrams near the right or left-hand axis. Thus in Figures 1 and 2, J will be considered to represent solutions containing impurity B in component A, while J_1 will represent solutions containing a small amount of A in B. From these figures, and from a study of other types of system, the important generalization emerges that k_1 is less than unity when the impurity depresses the melting point of the main component, and more than unity when it raises it. If the presence of impurity has no effect on the melting point of the main component, then k_1 is unity and no separation of the components is possible by zone refining. At the eutectic point C (Figure 1) k_1 is unity and the eutectic freezes without change of composition.

In practice, the solid and the liquid never reach equilibrium. Then an "effective distribution coefficient" (k) is relevant which is the actual ratio of the concentration of impurity in the solid that has just been deposited to its concentration in the liquid. It will usually lie between k_1 and unity and will, of course, approach k_1 as the rate of the zone movement is decreased. The substances to be refined often contain several impurites, but when only small traces of these are present, little interaction occurs among their molecules. Hence it is generally possible to consider effective distribution coefficients separately for each impurity.

C. OPERATING CHARACTERISTICS

The difference between zone refining and fractional crystallization lies in the mode of melting. Zone refining refers to a process in which a rod of impure material is purified by heating it so as to cause a molten zone to pass along its length (Figure 3). Thus, in zone refining, only a part of the material being purified is melted at any one time. Impurities tend to be carried forward in the molten zone. By repeating the process on the rod a number of times, a high degree of purification is possible (1 part in 10^9).



Source: Ref.2.

FIGURE 3 DIAGRAMMATIC REPRESENTATION OF A ZONE-REFINING EXPERIMENT

Zone melting can be carried out in a vertical or horizontal position. Although continuous operations are proposed, it is generally conducted on a batch scale. Apparatus is fairly simple. An ingot or sample container, a travel mechanism, and a source of heat are the basic requirements. In the case of solids melting below ambient, a means of refrigeration may be required. Construction and geometry of apparatus is varied to fit the specific process. Resistance, conduction, induction, radiation, electrical discharge, heat-transfer, hot-wire, etc.. are techniques utilized for heating. Pfann (Ref. 1) describes details of operation and equipment. Modifications to the zone refining technique are described in texts by Zief and Wilcox (Refs. 10 and 11).

A substance of the type represented by Figure 1 can, in theory, be purified by a single passage of the zone. If the initial composition is as represented by J, pure component A should crystallize from the back of the moving zone. This process should continue until the remaining part of the bar has the eutectic composition. In practice, however, liquid that contains some of the impurity is trapped in the growing crystals. Repetition, however, gives an increased purity that results in larger crystals, less impurity is trapped, and the purification becomes increasingly rapid.

Under given conditions, maximum separation would be obtained with an infinite number of zone passes, but from a practical point of view it is obviously important to know the smallest number that will achieve an adequate separation. The use of a narrow zone will give a high degree of purity; a wide zone will produce more rapid results. In practice, therefore, a wide zone is often used in the early stages, which are followed by the use of a zone whose length is, say, one-tenth that of the bar. If k is between 0.1 and 0.5, 20 passes will produce almost the maximum purification possible by this method; if it is very near to 1, hundreds of passes may be necessary.

Zone refining can be applied in theory to aqueous liquids and non-aqueous liquids, bulk solids, powders, slurries, colloids, salts, etc. However, the more complex the material the more difficult it will be to get efficient zone refining. Inherent viscosity and heat capacity parameters will also affect the zone refining operation. Viscous materials will not refine adequately and metals produce large heat losses. The main limitation besides a high cost of operation is slowness (in the order of mm/hr -- cm/hr).

Experimental work at DuPont (Ref. 13) on organic materials has been successful in purifying organic materials on a 10 kg scale (4" dia. pipe zone refiner). This work is covered by a patent (U.S. 3,844,724, October 29, 1974) and depends on insertion of metal heat conductors into the large mass of material being refined in order to obtain effective heat transfer. Large-scale operations would require internal heating.

III. APPLICATIONS TO DATE

A. HISTORICAL APPLICATIONS

As stated earlier, zone refining is a modern process. The pioneering paper, by Pfann, was published in 1952 (Ref. 6), and the first important application was to purify germanium for use in transistors. Alghough zone refining is applicable to many solid substances and some liquids, its use has been centered in inorganic/metallurgical applications requiring purification and crystal growth of metals, semiconductors, and inorganic chemicals. Present commercial applications are dominated by the semiconductor industry.

Classes of materials reported to be purified by zone refining are (Ref. 1):

1. **Elements** – Elements refined to high purity by zone refining include metals, and the semi-conductor elements, germanium and silicon. Reported elements include, Al, Sb, As, Be, Bi, B, Cd, Cr, Co, Cu, Gd, Ga, Ge, Au, In, Fe, Pb, Li, Mg, Mo, Ni, Cb, Pt, Pu, Rh, Si, Ag, Ta, Te, Sn, Ti, W, U, V, Y, Zn, Zr.

2. **Semiconducting and Intermetallic Compounds** – The binary and tertiary compounds are generally more difficult to refine than elements. Such materials include CdTe, HgTe, CdSb, ZnSb, Bi_2Te_3, CdS, ZnS, $ZnAs_2$, $CdIn_2Te_4$, $AgSbTe_2$, As_2SeTe_2, InSb-GaSb, AlSb-GaSb, $AuSb_2$, V_3Al, PtSn.

3. **Ionic Compounds, Oxides** – Much work has been done on alkali and alkaline earth metal oxides and salts, but the most extensively zone-refined ionic compounds are the halides. Ultrapure Group 3 metal halides have been required for semiconductor use. Pure forms of halides of Group 1 metals have been prepared for scintillation detectors. Zone refining has been applied to the metal oxides, barium compounds, and inorganic mixtures.

4. **Organic Compounds** – Zone refining has developed slowly in the field of organic chemistry, and, at present, its scope of application for commercial use is not known. It has been proposed for preparation of ultrapure pharmaceuticals and biological preparations. The potential for zone refining in this field is large. Many organic materials are reported to be purified in the laboratory through use of zone refining techniques. They include, for example, acenaphthene, acridine, acrylic acid, Aldrin, anthracene, carbazole, cetyl alcohol, chrysene, cresols, 2,4-dinitrotoluene, durene, hydroquinone, indole, Lindane, methyl methacrylate, naphthalene, nitroaniline, nitrophenol, phenol, pyrene, salicylic acid, stilbene, styrene, vanillin, etc.

Two efforts to use zone refining on a practical basis in the United States have been unsuccessful. One was an attempt to purify saline water. This effort failed because zone melting operations in this case involved excessive refrigeration costs and the distribution coefficient of salt in water is so low that a single bulk freezing step has the potential for doing the job without resorting to the expensive multiple freeze zone melting operations. Another was an attempt to separate heavy water from ordinary water. Here the distribution coefficient is close to unity which makes the zone refining operation unattractive for this operation.

Kuo and Wilcox describe research (Ref. 7) undertaken to provide information for design of industrial separation techniques utilizing pushing of foreign particles by solidification (e.g., horizontal zone melting with rotation). Test materials consisted of various mixtures of carbon particles, globules of copper, red ferric oxide, spherical silver and zinc, silicon in naphthalene, salol, and camphor. Pushing of these particles by a freezing interface was shown to be a complex process which is not yet fully understood. Bubbles, grain orientation, grain boundaries, container, and stirring were all shown to have a marked influence. Optimum and maximum pushing rate depended on tube diameter, particle-melt system, and on the exact shape and gas content of the zone. Application of zone refining to complex waste mixtures would presumably present more complex problems. No known waste streams, or industrial streams, are presently treated by zone refining.

B. POTENTIAL APPLICATION TO WASTE TREATMENT

Although many of the materials investigated in reported zone refining experiments can be termed "toxic," none constituted a hazardous waste product *per se*. No commercial or experimental applications of zone refining to conventional hazardous wastes are known.

Zone refining may have potential for processing small batches of high priority wastes if great purity is desirable and if operational costs can be justified. To be practical, these wastes would require a distribution coefficient < 1. Materials to be zone refined would likely be pure to start with. Toxic heavy metals, fluorides, oxides, PCB's, and chlorinated pesticides may be separable by zone refining, but work remains to be done to demonstrate feasibility. Highly complex or tertiary mixtures of materials would be difficult to separate, and work on such waste materials is most likely to proceed on an empirical basis. Highly viscous or polymeric materials, those that volatilize or degas, corrosive materials, explosive or pyrotechnic materials would not logically be refinable. At present, quantities would be limited to no more than 10 kg, and the process would be slow.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Zone refining is noted for its large energy requirements. Temperatures up to 3500°C are sometimes required and temperatures in the order of 2000°C are commonly used for purification of inorganics and elements; 500°C is considered a modest melting temperature for zone refining. Depending upon the required degree of purity and the value of the distribution coefficient, up to 100 passes through the heating zone may be required. The slower the movement of the zone (~ 2.5 cm/hour) the better the purification. This combination of high temperature, slow speed, and multiple passes add up to a large energy requirement. Heat loss from having high heat conductivity materials such as metals is prohibitive for large scale operation.

B. ENVIRONMENTAL IMPACTS

Besides the refined material itself and the impure portion of the core which is removed, the only direct emissions to be expected from zone refining are gases, water vapor, and decomposition products produced upon heating or "melting." These products can be expected to vary greatly depending upon the process, temperature, and materials being refined. Spent supports and refractory materials may accumulate, and heat will be dissipated from the system. It is unlikely that these emissions or by-products could be recycled or effectively used.

C. ECONOMIC ANALYSIS

No costs estimates for zone refining processes are available. Because of the obvious limitations of zone refining to waste processing, no attempt has been made to derive a cost analysis. However, it is known that heating and/or refrigeration costs have been traditionally high, and for this reason zone refining has not been an economically favorable process except where the need for ultra high purity materials justifies cost. Equipment is designed for a moderate to small sized operation. Although fairly simple in concept, a zone refining apparatus can be expected to be costly.

The cost for refining a $1.00/lb material could be prohibitive since the cost is related to cooling. If the material melts at -1°C then refrigeration is required which would add 15¢/lb. It would be cheaper to distill. If the melting point is 38-66°C, then tap water cooling might be sufficient to achieve a sufficient heat flux. Then 2¢/lb would be added. However, heat recovery is critical for an economic operation at higher temperature.

While distillation can never yield a 100 percent pure product, zone refining can give such a product if the mixture has a phase diagram of the type shown in Figure 1. Zone refining is usually more effective than distillation for materials that are already reasonably pure, say 99 percent. If the composition of the starting material is near the eutectic mixture, however, distillation may be more useful. Distillation has the advantage that it can treat tons of material in a continuous process, while present techniques in zone refining deal with only a few pounds at a time. Other techniques, such as liquid, gas, or ion-exchange chromatography, cannot produce absolutely pure materials, but are useful on very impure mixtures, and are, of course, valuable for thermally unstable organic substances. However, it is difficult to handle really large quantities of material by these latter methods also.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

This process has a demonstrated capability for producing very high purity materials, especially for the solid-state and semiconductor industries. Recent development work is aimed at using it for processing organic chemicals. It has potential for handling a variety of liquids, solids, sludges and slurries, at least in theory, provided they are categorized by a phase diagram. Gases, materials that decompose readily, or are highly viscous, are not treatable by zone refining.

However, as has been pointed out throughout, zone refining is slow, energy-intensive, and applicable to small batches. High costs and technical limitations in adapting the process to complex mixtures has discouraged general acceptance of zone melting as a common industrial method of purification. No large-scale, continuous zone refining apparatus suitable for waste treatment has been conceived and developed. Zone refining's forte appears to be in the specialized fields or industries which require high purity materials in small amounts, and for which a cost premium can be tolerated. Significant developments relating to waste processing do not appear to be forthcoming.

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